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(54) COMPOSITION OBJECT FOR CMP ABRASIVE PAD, CMP ABRASIVE PAD AND METHOD OF MAKING IT

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a composition object which can obtain a CMP abrasive pad excellent in alkali proof and acid proof and the CMP abrasive pad obtained from the composition object.

SOLUTION: This composition object for a CMP abrasive pad is constituted by including (A) an epoxy resin, (B) hardening agent, (C) hardening accelerator, and (D) bulking agent consisting of (d1) organic filler material and/or (d2) inorganic filler material. The CMP abrasive pad in this invention is manufactured by a method of manufacture compression molding a resin granule consisting of the composition object to be further not heated by a high frequency or compression molding a resin tablet consisting of the composition object to be further heated by the high frequency.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacturing method of the CMP scouring pad obtained from the constituent for CMP scouring pads which can obtain a suitable CMP scouring pad to specifically grind evenly the silicon wafer front face at the time of manufacturing a semiconductor integrated circuit about the CMP scouring pad obtained from the constituent for CMP scouring pads, and this constituent, and its manufacture approach, and this constituent, and this pad.

[0002]

[Background of the Invention] Integration and detailed-ization are progressing every year, in connection with it, the manufacturing technology of a large-scale integrated circuit carried out densification of the large-scale integrated circuit (LSI) represented by the latest semiconductor memory, and it has also complicated the production process. Furthermore, the number of laminatings of a semiconductor device is also increasing and, thereby, the irregularity on the front face of a semiconductor device used as a problem poses a problem conventionally. That is, when a semiconductor device front face is irregularity, it has led to generating of an open circuit, dispersion of resistance, etc.

[0003] Moreover, although lithography (projection exposure) is performed also with integration of a large-scale integrated circuit (LSI) as a pattern formation technique which forms the pattern of a mask in a wafer front face, by detailed-ization of a semiconductor integrated circuit in recent years, exposure wavelength becomes short and the depth of focus of an aligner is becoming very shallow further. Therefore, since it becomes impossible to resolve the pattern of a mask when irregularity exists in a wafer front face, flattening on the front face of a wafer is called for further.

[0004] Although the glass melt method, the spin-on glass method, etc. are used as a flattening technique on the front face of a wafer from the former, they are for mainly preventing an open circuit. Then, the approach of carrying out flattening of the wafer front face by the chemical mechanical polish (Chemical Mechanical Polishing (henceforth CMP)) technique is in use in recent years as an open circuit, dispersion of resistance, and an approach of solving the problem that a pattern is further unresolvable etc.

[0005] CMP which carries out flattening of the wafer front face is performed using the equipment shown in drawing 1. It consists of a wafer slewing gear 30 which has the rotating disc 10, and the electrode-holder plate 31 and a motor 32, the CMP scouring pad 20 is installed in the disc 10, and the dropping equipment 50 which trickles a slurry-like abrasive material on the CMP scouring pad 20 attaches the CMP equipment 1 shown in drawing 1. A wafer 40 is held at the electrode-holder plate 31, and the front face contacts the CMP scouring pad 20, and rotates it by the motor 32 further. The CMP scouring pad 20 rotates with a disc 10, grinds the front face of a wafer 40 by the abrasive material dropped on this pad 20 from dropping equipment 50, and carries out flattening of the wafer 40 front face.

[0006] Moreover, in order to form embedding wiring (DAMASHIN), CMP not only carries out flattening of the wafer front face, but is used. As a CMP scouring pad used for CMP, the pad which consists of current and foaming polyurethane is used. However, since flatness was using the

polyurethane in which it is bad and is foaming, abrasive powder tended to enter that detailed hole, and this pad had a problem of [in a pad] a lifting or a cone for blinding.

[0007] Furthermore, two, wiring (AL, W, etc.) and insulating layers (SiO₂ etc.), are mentioned as what is set as the object of CMP polish. The abrasive material used in case these two are ground uses the alkaline abrasive material whose pH is about 11, when grinding an insulating layer using the acid abrasive material whose pH is about three when pH differs greatly and grinds wiring. Therefore, the engine performance of alkali-proof and acid-proof both is required of a CMP scouring pad. In order to meet this demand, the scouring pad made of an epoxy resin is proposed (JP,11-138420,A).

[0008] However, the scouring pad made of this epoxy resin does not fully fill the engine performance of alkali-proof and acid-proof both, and further, since the manufacture approach of this scouring pad was an approach which fabricate by carrying out a notes form about the liquefied constituent for CMP scouring pads, it required the setting time of 5 - 12 hours per pad, and had the problem that the productivity of a CMP scouring pad was low.

[0009]

[Objects of the Invention] This invention tends to solve the problem in the conventional technique which was mentioned above, and aims at offering the manufacture approach of the constituent which can obtain the pad for CMP polish excellent in alkali resistance and acid resistance and the CMP scouring pad obtained from this constituent, and this pad that is further excellent in productivity.

[0010]

[Summary of the Invention] The constituent for CMP scouring pads concerning this invention is characterized by filler ** which consists of the (A) epoxy resin, the (B) curing agent, the (C) hardening accelerator and a (D) (d1) organic filler, and/or (d2) an inorganic filler containing. The above-mentioned organic filler (d1) is 0.01-20 micrometers in mean particle diameter measured by the Coulter counter method, and it is desirable to contain in 10 - 70% of the weight of the amount further in the constituent for CMP scouring pads (100 % of the weight).

[0011] The above-mentioned inorganic filler (d2) of consisting of quality of an inorganic fiber which is 1-30 micrometers in fiber length, and is 0.1-1 micrometer of diameters of fiber, and containing in 5 - 70% of the weight of the amount further in the constituent for CMP scouring pads (100 % of the weight) is also desirable. Moreover, it is desirable for the above-mentioned inorganic filler (d2) to consist of a non-subtlety particle which is the mean particle diameter of ten to 1x10³nm measured with the BET adsorption method, and to contain in 0.1 - 50% of the weight of the amount further in the constituent for CMP scouring pads (100 % of the weight).

[0012] Containing in 10 - 70% of the weight of the amount in the constituent for CMP scouring pads (100 % of the weight) also has the desirable filler (D) which consists of the above-mentioned organic filler (d1) and the above-mentioned inorganic filler (d2). The above-mentioned epoxy resin (A) of having two or more epoxy groups in a molecule is also desirable.

[0013] The above-mentioned curing agent (B) of their being phenol novolak resin or aralkyl phenol resin is also desirable. It is forming-from above-mentioned constituent for CMP scouring pads characterized by the CMP scouring pad concerning this invention. The manufacture approach of the CMP scouring pad concerning this invention is characterized by carrying out compression molding of the resin tablet which consisted of resin granulation which consists of the above-mentioned constituent for CMP scouring pads in a mould metal mold cavity, and is not heated by the RF, or the above-mentioned constituent for CMP scouring pads, and was heated by the RF.

[0014]

[Detailed Description of the Invention] Hereafter, the constituent for CMP scouring pads concerning this invention, a CMP scouring pad, and its manufacture approach are explained concretely. Filler ** which consists of the (A) epoxy resin, the (B) curing agent, the (C) hardening accelerator and a (D) (d1) organic filler, and/or (d2) an inorganic filler contains the constituent for CMP scouring pads concerning this invention.

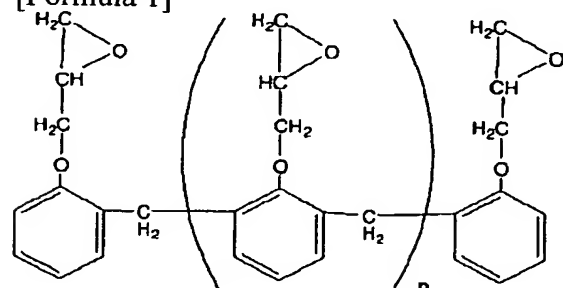
[0015] First, an epoxy resin (A) is explained below.

As an epoxy resin (A) used for <epoxy resin (A)> this invention Although not limited especially, the

epoxy resin which has two or more epoxy groups is used for intramolecular. As such a thing A novolak mold epoxy resin, a naphthalene mold epoxy resin, a biphenyl mold epoxy resin, A hydroquinone mold epoxy resin, a dicyclopentadiene mold epoxy resin, etc. can be mentioned. It is desirable the novolak mold epoxy resin preferably shown in the following chemical formula, a naphthalene mold epoxy resin, a biphenyl mold epoxy resin, and to use a novolak mold epoxy resin and a naphthalene mold epoxy resin preferably especially. these epoxy resins -- one sort -- or two or more sorts can be combined and it can use.

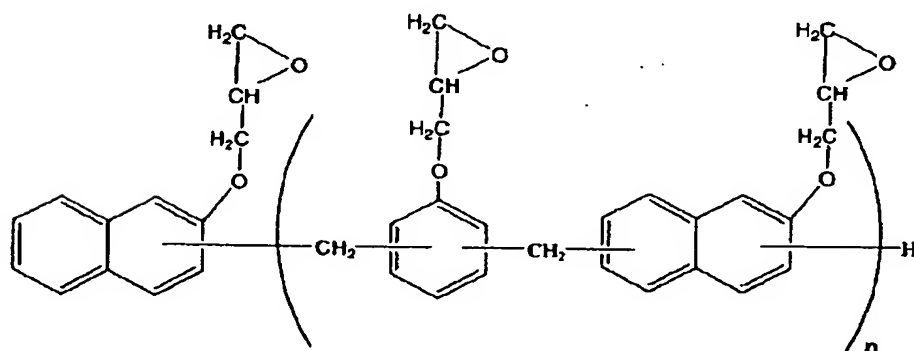
[0016]

[Formula 1]



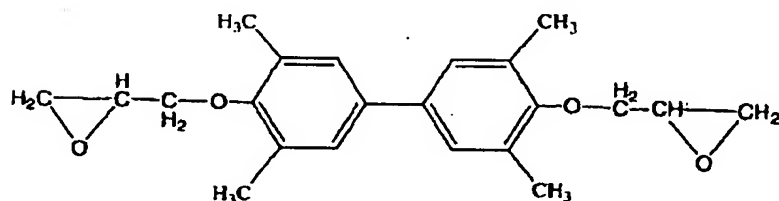
(n : 0 ~ 2)

<ノボラック型エポキシ樹脂>



(n : 0.35)

<ナフタレン型エポキシ樹脂>



<ビフェニル型エポキシ樹脂>

[0017] Specifically as a novolak mold epoxy resin shown in the above-mentioned chemical formula, YX-4000 (product made from oil-ized Shell Epoxy) etc. is mentioned as biphenyl mold epoxy resins,

such as NC7000L (Nippon Kayaku Co., Ltd. make), as naphthalene mold epoxy resins, such as EOCN102S, EOCN103S, and EOCN104S (Nippon Kayaku Co., Ltd. make).

[0018] As for the epoxy resin (A) used for this invention, it is desirable to contain in 20 - 60% of the weight of the amount preferably ten to 70% of the weight in the constituent for CMP scouring pads (100 % of the weight). Next, the curing agent (B) contained in the constituent for CMP scouring pads of this invention is explained below.

[0019] Especially as a curing agent (B) used for <curing agent (B)> this invention, although not limited, phenol novolak resin, aralkyl phenol resin, etc. are mentioned. When the CMP scouring pad which was excellent in alkali resistance and acid resistance when phenol novolak resin was added to the constituent for CMP scouring pads can be obtained and aralkyl phenol resin is added, it excels in alkali resistance and acid resistance, and the CMP scouring pad with which low absorptivity was given further can be obtained.

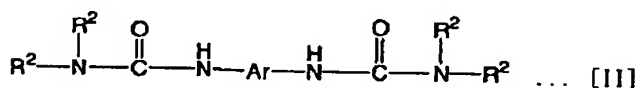
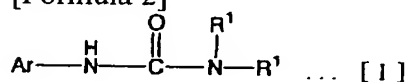
[0020] Specifically as such phenol novolak resin, MIREKKUSU XLC-3L (Mitsui Chemicals, Inc. make) etc. is mentioned as aralkyl phenol resin, such as PN-80 and PN-100 (Nippon Kayaku Co., Ltd. make). As for the above-mentioned curing agent (B), it is desirable to contain in 20 - 40% of the weight of the amount preferably ten to 50% of the weight in the constituent for CMP scouring pads (100 % of the weight).

[0021] When an epoxy resin (A) contains in the above-mentioned range and a curing agent (B) contains in the above-mentioned range further in the constituent for CMP scouring pads of this invention, the CMP scouring pad excellent in alkali resistance and acid resistance can be obtained. Furthermore, the hardening accelerator (C) contained in the constituent for CMP scouring pads of this invention is explained below.

[0022] As a hardening accelerator (C) used for <hardening-accelerator (C)> this invention Imidazole derivatives, such as 2-methylimidazole, 2-ethyl-4-methylimidazole, and a 2-ethyl-4-methylimidazole azine; Triphenyl phosphine, Organic phosphines, such as the Tori (p-methylphenyl) phosphine; 1, a 8-diaza cyclo (5, 4, 0) undecene-7 phenol salt, DBU derivatives, such as a 1, 8-diaza cyclo (5, 4, 0) undecene-7 phenol novolak salt, 1, and 8-diaza cyclo (5, 4, 0) undecene-7 phenol novolak carbonate; the urea derivative expressed with the following type [I] and [II] is mentioned.

[0023]

[Formula 2]



[0024] (the inside of a formula [I] and [II], and R1 and R2 -- an alkyl group -- preferably, especially, the alkyl group of carbon numbers 1-5 is expressed preferably, even if the same to mutual, you may differ and Ar expresses the alkyl group of carbon numbers 1-10, the permuted aryl group, or a non-permuted aryl group.)

In this invention, it is desirable to use the urea derivative expressed with 2-methylimidazole, 1, a 8-diaza cyclo (5, 4, 0) undecene-7 phenol novolak salt, and the above-mentioned formula [II] as a hardening accelerator (C).

[0025] As such 2-methylimidazole Specifically as a 1, such as 2MZ (Made in formation [Shikoku]), and 8-diaza cyclo (5, 4, 0) undecene-7 phenol novolak salt Specifically as a urea derivative expressed with the above-mentioned formulas [II], such as U-CAT-SA -831 and U-CAT-SA -841 (San Apro make), U-CAT-3502T (San Apro make) etc. are mentioned.

[0026] These hardening accelerators (C) are preferably added in the amount below the or more 0.1 10

weight section below the or more 0.1 20 weight section to the epoxy resin 100 weight section. By adding a hardening accelerator (C) with the above-mentioned compounding ratio, the reaction of an epoxy resin (A) and a curing agent (B) is promoted, and the effectiveness that the CMP scouring pad obtained is excellent in alkali resistance and acid resistance is acquired.

[0027] Furthermore, the filler (D) contained in the constituent for CMP scouring pads of this invention is explained below.

The filler (D) used for <filler (D)> this invention consists of an organic filler (d1) and/or an inorganic filler (d2). First, an organic filler (d1) is explained.

[0028] Especially as a <organic filler (d1)> above-mentioned organic filler (d1), although not limited, the organic filler 0.01-20 micrometers of whose mean particle diameter measured by the Coulter counter method are 0.1-3 micrometers preferably is desirable. It is desirable for macromolecule particles, such as a silicone rubber elastic body, a fluororesin, an aramid fiber, and polystyrene resin, to be mentioned, and to use a silicone rubber elastic body preferably as such an organic filler (d1). one sort as which this organic filler (d1) is chosen from these -- or two or more sorts can be combined and it can use.

[0029] When the filler (D) used for this invention consists of an organic filler (d1), as for an organic filler (d1), it is desirable to contain in 15 - 50% of the weight of the amount preferably ten to 70% of the weight in the constituent for CMP scouring pads (100 % of the weight). By containing the organic filler (d1) of the above-mentioned particle diameter range in the above-mentioned range, flexibility is given to a CMP scouring pad and the breakage when installing in deformation of the pad after a mould and polish equipment can be prevented. Furthermore, it is possible to adjust the degree of hardness of a CMP scouring pad front face, and, thereby, the effect on the polish effectiveness by the variation in the particle size of the abrasive material used for CMP polish can be prevented.

[0030] Moreover, it is desirable to use an epoxy group content silicone rubber elastic body still more preferably as the above-mentioned silicone rubber elastic body. Specifically as an epoxy group content silicone rubber elastic body, TOREFIRU E-601 (Dow Corning Toray Silicone make) etc. is mentioned. When an epoxy group content silicone rubber elastic body contains in the constituent for CMP scouring pads, the CMP scouring pad obtained from this elastic body having the good dispersibility to the inside of a constituent is formed into low elasticity, the stress after this pad shaping can be eased by it, and the effectiveness that the flatness of this pad improves further is acquired.

[0031] Especially as a <inorganic filler (d2)> above-mentioned inorganic filler (d2), although not limited, the quality of an inorganic fiber, a non-subtlety particle, etc. are mentioned. this inorganic filler (d2) has these independent -- or it comes to be mixed As the above-mentioned quality of an inorganic fiber (d2), the quality of an inorganic fiber the diameter of fiber measured from the SEM photograph is [0.1-1 micrometer of 0.1-0.5 micrometers of 1-30 micrometers of whose fiber length] 1-20 micrometers preferably further is desirable.

[0032] It is desirable for calcium silicate, a potassium titanate whisker, a silicon carbide whisker, a glass fiber, a carbon fiber, etc. to be mentioned, among these to use calcium silicate and a potassium titanate whisker preferably as such quality of an inorganic fiber (d2). This quality of an inorganic fiber (d2) consists of one sort chosen from these, or two sorts or more.

[0033] Specifically as the above-mentioned calcium silicate, TISUMO D, TISUMO N (product made from Otsuka Chemistry), etc. are mentioned as potassium titanate whiskers, such as ZONOHAIJI and Moss Heidi (Ube Material Industries make). The filler (D) used for this invention consists of an inorganic filler (d2), and when an inorganic filler (d2) is the quality of an inorganic fiber, as for such quality of an inorganic fiber, it is desirable to contain in 10 - 50% of the weight of the amount preferably five to 70% of the weight in the constituent for CMP scouring pads (100 % of the weight). The mechanical strength of the pad for CMP polish obtained by containing the inorganic fiber in the above-mentioned diameter range of fiber and the fiber length range in the above-mentioned range can improve, and when molding shrinkage becomes low further, the breakage at the time of this pad deformation after a mould and handling can be prevented. Furthermore, the alkali resistance and acid resistance of a CMP scouring pad improve, and adjustment of surface hardness is still also attained.

[0034] Moreover, the mean particle diameter measured with the BET adsorption method has [the non-

subtlety particle used as the above-mentioned inorganic filler (d2)] a ten to 1×10^2 nm preferably desirable non-subtlety particle ten to 1×10^3 nm. It is desirable to mention metallic oxides, such as a silicon dioxide, titanium oxide, an aluminum oxide, and yttrium oxide, and a multiple oxide ultrafine particle, and for a silicon dioxide to use preferably as such a non-subtlety particle. This non-subtlety particle consists of one sort chosen from these, or two sorts or more. Specifically as the above-mentioned silicon dioxide, Nanotech (C.I. Kasei make) etc. is mentioned.

[0035] The filler (D) used for this invention consists of an inorganic filler (d2), and when an inorganic filler (d2) is a non-subtlety particle, as for such a non-subtlety particle, it is desirable to contain in 1 - 30% of the weight of the amount preferably 0.1 to 50% of the weight in the constituent for CMP scouring pads (100 % of the weight). In addition to the above-mentioned effectiveness in the case of adding an inorganic fiber by adding the non-subtlety particle of the above-mentioned particle diameter range in the above-mentioned range, since it is a particle, the surface flatness of a pad improves, and in case it is CMP polish, it becomes possible to reduce the probability to give a blemish to a wafer.

[0036] Furthermore, it sets to this invention. An inorganic filler (d2) You may consist of quality of an inorganic fiber, and a non-subtlety particle, and the quality of an inorganic fiber is 35 - 65% of the weight of an amount preferably five to 95% of the weight in that case in an inorganic filler (d2) (the total quantity of the quality of an inorganic fiber and a non-subtlety particle is 100 % of the weight). It is desirable for a non-subtlety particle to consist of 35 - 65% of the weight of an amount preferably five to 95% of the weight. Furthermore, as for the inorganic filler (d2) which consists of quality of an inorganic fiber, and a non-subtlety particle, it is desirable to contain in 20 - 50% of the weight of the amount preferably 15 to 70% of the weight in the constituent for CMP scouring pads (100 % of the weight).

[0037] By adding these inorganic fillers (d2) in the above-mentioned amount, contraction of a CMP scouring pad becomes small and flatness, alkali resistance, and acid resistance improve. Moreover, when the filler (D) used for this invention consists of the above-mentioned organic filler (d1) and the above-mentioned inorganic filler (d2), it is desirable in a filler (D) (100 % of the weight) for an organic filler (d1) to be 20 - 60% of the weight of an amount preferably five to 95% of the weight, and for the inorganic filler (d2) to contain it in 40 - 80% of the weight of the amount preferably five to 95% of the weight.

[0038] Furthermore, when a filler (D) consists of the above-mentioned organic filler (d1) and an inorganic filler (d2), it is also preferably desirable [a filler (D)] in the constituent for CMP scouring pads (100 % of the weight) to contain in 10 - 50% of the weight of the amount ten to 70% of the weight. When such a filler (D) contains in the above-mentioned range in the constituent for CMP scouring pads, the surface hardness of a CMP scouring pad, mechanical strength, deformation, and adjustment of smoothness are possible, and the presentation can be properly used suitably with the size for polish.

[0039] In <other filler> this invention, a release agent, a silane coupling agent, a flame retarder, a coloring agent, a low stress-sized agent, a filler, etc. can be added to the constituent for CMP scouring pads of this invention if needed. As the above-mentioned release agent, metallic soap, such as metal salt; zinc stearate of higher fatty acids, such as ester wax; behenic acid zinc of higher fatty acids [, such as higher-fatty-acid; carnauba wax], such as a montanoic acid, stearin acid, behenic acid, and oleic acid, zinc oleate, barium stearate, magnesium stearate, and aluminum stearate, can be mentioned, and one sort chosen from these or two sorts or more can be added.

[0040] Moreover, as the above-mentioned silane coupling agent, carbon black, a phthalocyanine, etc. can mention [a bromine-ized epoxy resin, an antimony trioxide an aluminum hydroxide etc.] butadiene rubber etc. for beta-(3, 4 epoxycyclohexyl) ethyltrimethoxysilane, gamma-glycidoxypropyltrimetoxysilane, etc. as a low stress-sized agent as the above-mentioned coloring agent as the above-mentioned flame retarder.

[0041] [Constituent for CMP scouring pads] The above-mentioned bulking agent (D) ** which consists of an epoxy resin (A), a curing agent (B), a hardening accelerator (C) and (d1) an organic filler, and/or (d2) an inorganic filler contains the constituent for CMP scouring pads concerning this invention. Therefore, as a mode of the constituent for CMP scouring pads concerning this invention, the following constituents are mentioned, for example.

- (1) The constituent for CMP scouring pads containing an epoxy resin (A), a curing agent (B), a hardening accelerator (C), and the bulking agent (D) that consists of an organic filler (d1).
- (2) The constituent for CMP scouring pads containing an epoxy resin (A), a curing agent (B), a hardening accelerator (C), and the bulking agent (D) that consists of an inorganic filler (d2).
- (3) The constituent for CMP scouring pads containing the bulking agent (D) which consists of an epoxy resin (A), a curing agent (B), a hardening accelerator (C), an organic filler (d1), and an inorganic filler (d2).

[0042] The CMP scouring pad obtained from this constituent when the constituent for CMP scouring pads concerning this invention is either of (1) - (3) and each constituent is an above-mentioned presentation rate is excellent in alkali resistance and acid resistance, further, since it can manufacture a CMP scouring pad by compression molding according to this constituent, can be cast in a short time compared with the manufacture depended on the conventional notes form, and is excellent also in the productivity of a CMP scouring pad.

[0043] [CMP scouring pad] The CMP scouring pad concerning this invention is manufactured by the following approach using the above-mentioned constituent for CMP scouring pads. Usually, thickness of a diameter is large at about 1mm, and a CMP scouring pad is manufactured by 350mm. An example (the thickness of 1.2mm, diameter of 350mm) of the CMP scouring pad of this invention is shown in drawing 2.

[0044] In such a CMP scouring pad, although the content of the constituent in the constituent for CMP scouring pads can adjust the surface hardness and flatness, in this invention, it is desirable to adjust the content of a constituent so that surface hardness may be obtained by the BIKKAZU degree of hardness and 2-40, and 20-100 micrometers of flatness preferably measured by 4-30, and the three-dimensions measuring method may be preferably obtained by 30-70 micrometers.

[0045] The [manufacture approach of a CMP scouring pad] The manufacture approach of the CMP scouring pad concerning this invention is shown hereafter. A CMP scouring pad is manufactured by carrying out compression molding of the resin tablet which consisted of resin granulation which the manufacture approach of a CMP scouring pad consists of the above-mentioned constituent for CMP scouring pads in a mould metal mold cavity, and is not heated by the RF, or this constituent for CMP scouring pads, and was heated by the RF.

[0046] The resin granulation which carries out heating kneading, cools and grinds continuously the epoxy group content compound mentioned above, a curing agent, a hardening accelerator, an organic filler and/or an inorganic filler, and the constituent for CMP scouring pads that contains the silane coupling agent further by 2 rolls after mixing or the kneader with mixers, such as a Henschel mixer and a ribbon blender, and does not specifically heat it by the RF probably is obtained. Or further, this resin granulation is tablet-sized with a tableting press, it heats by high frequency with a high-frequency-preheating machine, and a resin tablet is obtained.

[0047] Next, the resin tablet heated by the above-mentioned high frequency or the resin granulation which is not heated by high frequency is placed using the compression molding equipment shown in drawing 2 on the molding-under molding metal mold heated by 170 degrees C metal mold 61.

Furthermore, after putting the top molding metal mold 63, it compresses by performing hot press with the movable base 64, and compression molding of the pad constituent for CMP polish is carried out in the cavity section 65 between the bottom molding metal mold 61 and the top molding metal mold 63. After resin's hardening, the top molding metal mold 63 and the periphery ring 62 are removed, after cooling the hardened sheet in Ayr, it takes out and the CMP scouring pad concerning this invention is obtained.

[0048] Usually, the general manufacture approach of a CMP scouring pad heats by the RF what tablet-sized the constituent for CMP scouring pads at the room temperature, and is performed by the approach of transfer-molding. However, when manufacturing a pad by this shaping approach, in order that the gate may be needed for the product section of a manufacturing installation and the transfer pressure of a constituent may concentrate near [that] the gate, consistency variation becomes large in the manufactured pad, and the obtained CMP scouring pad is [become] easy to deform. However,

according to the manufacture approach of the CMP scouring pad applied to this invention which manufactures a CMP scouring pad by compression molding using the constituent for CMP scouring pads of this invention, the gate is not required for the product section of a manufacturing installation, and further, when a pressure joins homogeneity, the thing of the CMP scouring pad with little deformation can be obtained and carried out to the whole constituent.

[0049]

[Effect of the Invention] If this invention is caused, the manufacture approach of the constituent which can obtain the CMP scouring pad excellent in alkali resistance and acid resistance and the CMP scouring pad obtained from this constituent, and this pad that is further excellent in productivity can be offered.

[0050]

[Example] Hereafter, although this invention is explained still more concretely based on an example, this invention is not limited to these examples. In addition, the CMP scouring pad obtained in the example and the example of a comparison was evaluated according to the following approaches. The flatness of the flatness pad of a pad was measured using three coordinate measuring machine GC [by Tokyo Seimitsu Co., Ltd.]-1000D. Measurement was performed by measuring a pad flat surface 20 point contact under the environment of 23 degrees C and 53%RH.

The chemical resistance of a chemical corrosion resistance test scouring pad was immersed in the KOH water solution of pH12, and the HCl/H₂O₂ mixing water solution of pH2 at 60 degrees C in the scouring pad for 5 hours, asked for weight rate-of-change:% of the scouring pad by the following formula, and evaluated the chemical resistance of a scouring pad from this weight rate of change.

[0051]

[Equation 1]

$$\frac{\text{浸漬後の研磨パッドの重量} - \text{浸漬前の研磨パッドの重量}}{\text{浸漬前の研磨パッドの重量}} \times 100$$

[0052]

[Example 1] The naphthalene mold epoxy resin (trade name; NC7000L, Nippon Kayaku Co., Ltd. make) 120 weight section, The aralkyl phenol resin (trade name ;P N-80, Nippon Kayaku Co., Ltd. make) 94 weight section, The 2-methylimidazole (Made in formation [Trade name; 2MZ, Shikoku]) 0.4 weight section, Potassium titanate whisker [(trade name; TISUMO D, product made from Otsuka Chemistry), 15 micrometers of mean fiber length, the 0.5 micrometer (it measures from SEM photograph)] 170 weight section of diameters of average fiber, After mixing the constituent for CMP scouring pads containing the gamma-glycidoxypolytrimetoxysilane (trade name; KBM-403, product made from Shin-etsu Chemistry) 0.5 weight section, and the carnauba wax 2 weight section with a Henschel mixer, it kneaded for 2 minutes with 2 rolls heated at 90 degrees C. Then, the resin granulation which cools at a room temperature, grinds on 5mm mesh screen with a power mill, and is not heated by the RF was obtained. This resin granulation was placed on molding-under compression molding metal mold metal mold, compression molding was carried out on conditions with a clamping pressure of 35t for [die-temperature / of 170 degrees C /, and compression (metal mold close) time amount] 120 seconds, and the scouring pad with 1.2mm [in thickness] and a diameter of 350mm was created.

[0053] The pad flatness of the obtained scouring pad and a chemical corrosion resistance test were evaluated according to the above-mentioned approach. A result is shown in a table 1.

[0054]

[Example 2] The scouring pad was created like the example 1 except having changed the potassium titanate whisker 170 weight section of an example 1 into the fiber length of 3 micrometers, and [(trade name; ZONOHAIJI, Ube Material Industries make) 0.3 micrometer [of calcium silicate diameters of fiber] (it measuring with SEM photograph)] 170 weight section.

[0055] The pad flatness of the obtained scouring pad and a chemical corrosion resistance test were evaluated according to the above-mentioned approach. A result is shown in a table 1.

[0056]

[Example 3] It replaced with the potassium titanate whisker 170 weight section of an example 1, and the

scouring pad was created like the example 1 except having added the silicon-dioxide [(trade name; Nanotech and C.I. Kasei make) mean particle diameter of 12nm (it measures with BET adsorption method)] 60 weight section.

[0057] The pad flatness of the obtained scouring pad and a chemical corrosion resistance test were evaluated according to the above-mentioned approach. A result is shown in a table 1.

[0058]

[Example 4] The potassium titanate whisker and gamma-glycidoxypyrtrimetoxysilane of an example 1 were made additive-free (0 weight section), and the scouring pad was created like the example 1 except having added the silicone rubber [(trade name; TOREFIRU E-601, Toray Industries Dow Corning make) mean particle diameter of 2 micrometers (it measures by Coulter counter method)] 160 weight section.

[0059] The pad flatness of the obtained scouring pad and a chemical corrosion resistance test were evaluated according to the above-mentioned approach. A result is shown in a table 1.

[0060]

[Example 5] The potassium titanate whisker 170 weight section of an example 1 was made into 40 weight sections, the silicone rubber 100 weight section was added further, and the scouring pad was created like the example 1 except having made the gamma-glycidoxypyrtrimetoxysilane 0.5 weight section into the 0.2 weight section.

[0061] The pad flatness of the obtained scouring pad and a chemical corrosion resistance test were evaluated according to the above-mentioned approach. A result is shown in a table 1.

[0062]

[The example 1 of a comparison] According to the conditions of an example 1, the scouring pad was created using the naphthalene mold epoxy resin 120 weight section, the aralkyl phenol resin 94 weight section, the imidazole 0.4 weight section, and the carnauba wax 2 weight section. The pad flatness of the obtained scouring pad and a chemical corrosion resistance test were evaluated according to the above-mentioned approach. A result is shown in a table 1.

[0063]

[The example 2 of a comparison] After mixing the constituent which consists of the bisphenol A mold epoxy resin (trade name; Epicoat 828, product made from oil-ized Shell Epoxy) 100 weight section, and the diamino bibenzyl 24 weight section by the Shinagawa mixer, a notes form is carried out into the metal mold shown in drawing 3 , and it heated for 5 hours and was made to harden at 120 degrees C. Ejection and a scouring pad were created from metal mold after cooling.

[0064] The pad flatness of the obtained scouring pad and a chemical corrosion resistance test were evaluated according to the above-mentioned approach. A result is shown in a table 1.

[0065]

[A table 1]

	実施例1		実施例2		実施例3		実施例4		実施例5		比較例1		比較例2	
1. 研磨パッド組成物	重量部	(重量%)	重量部	(重量%)	重量部	(重量%)	重量部	(重量%)	重量部	(重量%)	重量部	(重量%)	重量部	(重量%)
<エポキシ樹脂>														
ナフレン型エポキシ樹脂	120.0	(31.02)	120.0	(31.02)	120.0	(43.34)	120.0	(31.88)	120.0	(33.65)	120.0	(55.45)		
ビスフェノールA型エポキシ樹脂													100.0	(80.65)
<硬化剤>														
アラルキルフェノール樹脂	94.0	(24.30)	94.0	(24.30)	94.0	(33.95)	94.0	(24.97)	94.0	(26.36)	94.0	(43.44)		
ジメチルフェニルメタン													24.0	(19.65)
<硬化促進剤>														
2-メチルイミダゾール	0.4	(0.10)	0.4	(0.10)	0.4	(0.14)	0.4	(0.11)	0.4	(0.11)	0.4	(0.18)		
<無機充填材>														
チタン酸カルウムワイスカー	170.0	(43.93)							40.0	(11.22)				
カルシウムシリケート			170.0	(43.93)										
二酸化ケイ素					60.0	(21.67)								
<有機充填材>														
シリコンゴム							160.0	(42.51)	100.0	(28.04)				
アークリルキシプロピルトリメチルシリラン	0.5	(0.13)	0.5	(0.13)	0.5	(0.18)			0.2	(0.06)				
カルナバワックス	2.0	(0.52)	2.0	(0.52)	2.0	(0.72)	2.0	(0.53)	2.0	(0.56)	2.0	(0.92)		
合 計	386.9	(100.00)	386.9	(100.00)	276.9	(100.00)	378.4	(100.00)	356.8	(100.00)	216.4	(100.00)	124.0	(100.00)
2. 研磨パッドの成形条件														
2.1. 成形法	圧縮成形		圧縮成形		圧縮成形		圧縮成形		圧縮成形		圧縮成形		注 射	
2.1. 成形時間 * 1	120秒間		120秒間		120秒間		120秒間		120秒間		120秒間		5時間	
3. 研磨パッドの特性														
3.1. ノッド平面度: μm	60		85		50		50		30		500		—	
3.2. 耐薬品性試験														
①重量変化率(HCl/H ₂ O ₂): %	0.6		0.6		0.7		0.5		0.6		0.9		0.9	
②重量変化率(KOH): %	0.4		0.4		0.5		0.4		0.4		0.8		0.7	

* 1: 実施例1～比較例1までは金型が閉じている時間、比較例2は硬化するまでの時間を示す。

[Translation done.]

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

TECHNICAL FIELD

[Field of the Invention] This invention relates to the manufacturing method of the CMP scouring pad obtained from the constituent for CMP scouring pads which can obtain a suitable CMP scouring pad to specifically grind evenly the silicon wafer front face at the time of manufacturing a semiconductor integrated circuit about the CMP scouring pad obtained from the constituent for CMP scouring pads, and this constituent, and its manufacture approach, and this constituent, and this pad.

[0002]

[Background of the Invention] Integration and detailed-ization are progressing every year, in connection with it, the manufacturing technology of a large-scale integrated circuit carried out densification of the large-scale integrated circuit (LSI) represented by the latest semiconductor memory, and it has also complicated the production process. Furthermore, the number of laminatings of a semiconductor device is also increasing and, thereby, the irregularity on the front face of a semiconductor device used as a problem poses a problem conventionally. That is, when a semiconductor device front face is irregularity, it has led to generating of an open circuit, dispersion of resistance, etc.

[0003] Moreover, although lithography (projection exposure) is performed also with integration of a large-scale integrated circuit (LSI) as a pattern formation technique which forms the pattern of a mask in a wafer front face, by detailed-ization of a semiconductor integrated circuit in recent years, exposure wavelength becomes short and the depth of focus of an aligner is becoming very shallow further. Therefore, since it becomes impossible to resolve the pattern of a mask when irregularity exists in a wafer front face, flattening on the front face of a wafer is called for further.

[0004] Although the glass melt method, the spin-on glass method, etc. are used as a flattening technique on the front face of a wafer from the former, they are for mainly preventing an open circuit. Then, the approach of carrying out flattening of the wafer front face by the chemical mechanical polish (Chemical Mechanical Polishing (henceforth CMP)) technique is in use in recent years as an open circuit, dispersion of resistance, and an approach of solving the problem that a pattern is further unresolvable etc.

[0005] CMP which carries out flattening of the wafer front face is performed using the equipment shown in drawing 1. It consists of a wafer slewing gear 30 which has the rotating disc 10, and the electrode-holder plate 31 and a motor 32, the CMP scouring pad 20 is installed in the disc 10, and the dropping equipment 50 which trickles a slurry-like abrasive material on the CMP scouring pad 20 attaches the CMP equipment 1 shown in drawing 1. A wafer 40 is held at the electrode-holder plate 31, and the front face contacts the CMP scouring pad 20, and rotates it by the motor 32 further. The CMP scouring pad 20 rotates with a disc 10, grinds the front face of a wafer 40 by the abrasive material dropped on this pad 20 from dropping equipment 50, and carries out flattening of the wafer 40 front face.

[0006] Moreover, in order to form embedding wiring (DAMASHIN), CMP not only carries out flattening of the wafer front face, but is used. As a CMP scouring pad used for CMP, the pad which consists of current and foaming polyurethane is used. However, since flatness was using the polyurethane in which it is bad and is foaming, abrasive powder tended to enter that detailed hole, and this pad had a problem of [in a pad] a lifting or a cone for blinding.

[0007] Furthermore, two, wiring (AL, W, etc.) and insulating layers (SiO₂ etc.), are mentioned as what is set as the object of CMP polish. The abrasive material used in case these two are ground uses the alkaline abrasive material whose pH is about 11, when grinding an insulating layer using the acid abrasive material whose pH is about three when pH differs greatly and grinds wiring. Therefore, the engine performance of alkali-proof and acid-proof both is required of a CMP scouring pad. In order to meet this demand, the scouring pad made of an epoxy resin is proposed (JP,11-138420,A).

[0008] However, the scouring pad made of this epoxy resin does not fully fill the engine performance of alkali-proof and acid-proof both, and further, since the manufacture approach of this scouring pad was an approach which fabricate by carrying out a notes form about the liquefied constituent for CMP scouring pads, it required the setting time of 5 - 12 hours per pad, and had the problem that the productivity of a CMP scouring pad was low.

[0009]

[Objects of the Invention] This invention tends to solve the problem in the conventional technique which was mentioned above, and aims at offering the manufacture approach of the constituent which can obtain the pad for CMP polish excellent in alkali resistance and acid resistance and the CMP scouring pad obtained from this constituent, and this pad that is further excellent in productivity.

[0010]

[Summary of the Invention] The constituent for CMP scouring pads concerning this invention is characterized by filler ** which consists of the (A) epoxy resin, the (B) curing agent, the (C) hardening accelerator and a (D) (d1) organic filler, and/or (d2) an inorganic filler containing. The above-mentioned organic filler (d1) is 0.01-20 micrometers in mean particle diameter measured by the Coulter counter method, and it is desirable to contain in 10 - 70% of the weight of the amount further in the constituent for CMP scouring pads (100 % of the weight).

[0011] The above-mentioned inorganic filler (d2) of consisting of quality of an inorganic fiber which is 1-30 micrometers in fiber length, and is 0.1-1 micrometer of diameters of fiber, and containing in 5 - 70% of the weight of the amount further in the constituent for CMP scouring pads (100 % of the weight) is also desirable. Moreover, it is desirable for the above-mentioned inorganic filler (d2) to consist of a non-subtlety particle which is the mean particle diameter of ten to 1x10³nm measured with the BET adsorption method, and to contain in 0.1 - 50% of the weight of the amount further in the constituent for CMP scouring pads (100 % of the weight).

[0012] Containing in 10 - 70% of the weight of the amount in the constituent for CMP scouring pads (100 % of the weight) also has the desirable filler (D) which consists of the above-mentioned organic filler (d1) and the above-mentioned inorganic filler (d2). The above-mentioned epoxy resin (A) of having two or more epoxy groups in a molecule is also desirable.

[0013] The above-mentioned curing agent (B) of their being phenol novolak resin or aralkyl phenol resin is also desirable. It is forming-from above-mentioned constituent for CMP scouring pads characterized by the CMP scouring pad concerning this invention. The manufacture approach of the CMP scouring pad concerning this invention is characterized by carrying out compression molding of the resin tablet which consisted of resin granulation which consists of the above-mentioned constituent for CMP scouring pads in a mould metal mold cavity, and is not heated by the RF, or the above-mentioned constituent for CMP scouring pads, and was heated by the RF.

[0014]

[Detailed Description of the Invention] Hereafter, the constituent for CMP scouring pads concerning this invention, a CMP scouring pad, and its manufacture approach are explained concretely. Filler ** which consists of the (A) epoxy resin, the (B) curing agent, the (C) hardening accelerator and a (D) (d1) organic filler, and/or (d2) an inorganic filler contains the constituent for CMP scouring pads concerning this invention.

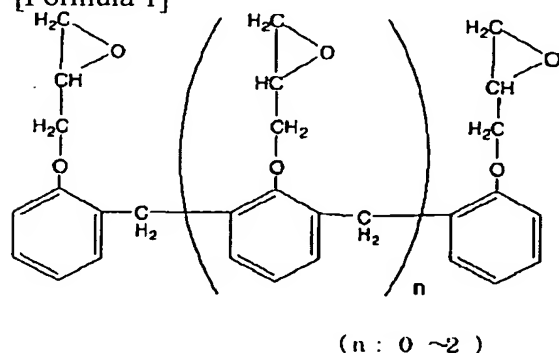
[0015] First, an epoxy resin (A) is explained below.

As an epoxy resin (A) used for <epoxy resin (A)> this invention Although not limited especially, the epoxy resin which has two or more epoxy groups is used for intramolecular. As such a thing A novolak mold epoxy resin, a naphthalene mold epoxy resin, a biphenyl mold epoxy resin, A hydroquinone mold

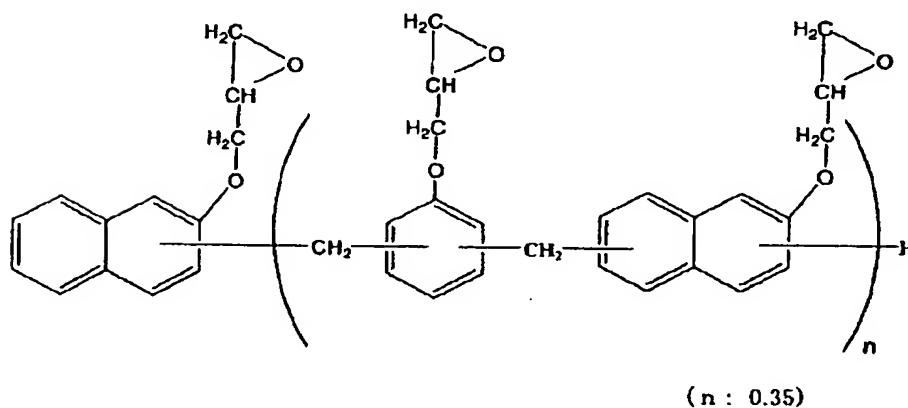
epoxy resin, a dicyclopentadiene mold epoxy resin, etc. can be mentioned. It is desirable the novolak mold epoxy resin preferably shown in the following chemical formula, a naphthalene mold epoxy resin, a biphenyl mold epoxy resin, and to use a novolak mold epoxy resin and a naphthalene mold epoxy resin preferably especially. these epoxy resins -- one sort -- or two or more sorts can be combined and it can use.

[0016]

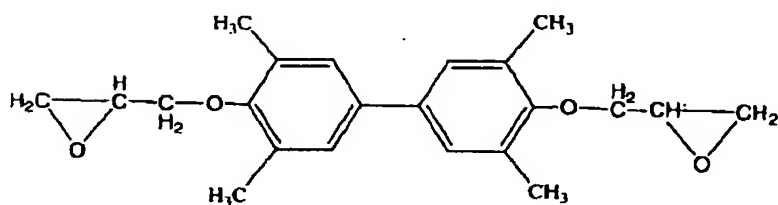
[Formula 1]



<ノボラック型エポキシ樹脂>



<ナフタレン型エポキシ樹脂>



<ビフェニル型エポキシ樹脂>

[0017] Specifically as a novolak mold epoxy resin shown in the above-mentioned chemical formula, YX-4000 (product made from oil-ized Shell Epoxy) etc. is mentioned as biphenyl mold epoxy resins, such as NC7000L (Nippon Kayaku Co., Ltd. make), as naphthalene mold epoxy resins, such as EOCN102S, EOCN103S, and EOCN104S (Nippon Kayaku Co., Ltd. make).

[0018] As for the epoxy resin (A) used for this invention, it is desirable to contain in 20 - 60% of the weight of the amount preferably ten to 70% of the weight in the constituent for CMP scouring pads (100 % of the weight). Next, the curing agent (B) contained in the constituent for CMP scouring pads of this invention is explained below.

[0019] Especially as a curing agent (B) used for <curing agent (B)> this invention, although not limited, phenol novolak resin, aralkyl phenol resin, etc. are mentioned. When the CMP scouring pad which was excellent in alkali resistance and acid resistance when phenol novolak resin was added to the constituent for CMP scouring pads can be obtained and aralkyl phenol resin is added, it excels in alkali resistance and acid resistance, and the CMP scouring pad with which low absorptivity was given further can be obtained.

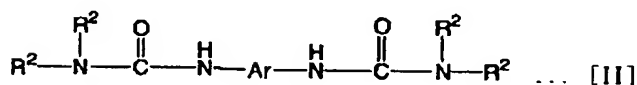
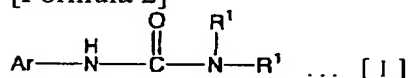
[0020] Specifically as such phenol novolak resin, MIREKKUSU XLC-3L (Mitsui Chemicals, Inc. make) etc. is mentioned as aralkyl phenol resin, such as PN-80 and PN-100 (Nippon Kayaku Co., Ltd. make). As for the above-mentioned curing agent (B), it is desirable to contain in 20 - 40% of the weight of the amount preferably ten to 50% of the weight in the constituent for CMP scouring pads (100 % of the weight).

[0021] When an epoxy resin (A) contains in the above-mentioned range and a curing agent (B) contains in the above-mentioned range further in the constituent for CMP scouring pads of this invention, the CMP scouring pad excellent in alkali resistance and acid resistance can be obtained. Furthermore, the hardening accelerator (C) contained in the constituent for CMP scouring pads of this invention is explained below.

[0022] As a hardening accelerator (C) used for <hardening-accelerator (C)> this invention Imidazole derivatives, such as 2-methylimidazole, 2-ethyl-4-methylimidazole, and a 2-ethyl-4-methylimidazole azine; Triphenyl phosphine, Organic phosphines, such as the Tori (p-methylphenyl) phosphine; 1, a 8-diaza cyclo (5, 4, 0) undecene-7 phenol salt, DBU derivatives, such as a 1, 8-diaza cyclo (5, 4, 0) undecene-7 phenol novolak salt, 1, and 8-diaza cyclo (5, 4, 0) undecene-7 phenol novolak carbonate; the urea derivative expressed with the following type [I] and [II] is mentioned.

[0023]

[Formula 2]



[0024] (the inside of a formula [I] and [II], and R1 and R2 -- an alkyl group -- preferably, especially, the alkyl group of carbon numbers 1-5 is expressed preferably, even if the same to mutual, you may differ and Ar expresses the alkyl group of carbon numbers 1-10, the permuted aryl group, or a non-permuted aryl group.)

In this invention, it is desirable to use the urea derivative expressed with 2-methylimidazole, 1, a 8-diaza cyclo (5, 4, 0) undecene-7 phenol novolak salt, and the above-mentioned formula [II] as a hardening accelerator (C).

[0025] As such 2-methylimidazole Specifically as a 1, such as 2MZ (Made in formation [Shikoku]), and 8-diaza cyclo (5, 4, 0) undecene-7 phenol novolak salt Specifically as a urea derivative expressed with the above-mentioned formulas [II], such as U-CAT-SA -831 and U-CAT-SA -841 (San Apro make), U-CAT-3502T (San Apro make) etc. are mentioned.

[0026] These hardening accelerators (C) are preferably added in the amount below the or more 0.1 10 weight section below the or more 0.1 20 weight section to the epoxy resin 100 weight section. By adding a hardening accelerator (C) with the above-mentioned compounding ratio, the reaction of an

epoxy resin (A) and a curing agent (B) is promoted, and the effectiveness that the CMP scouring pad obtained is excellent in alkali resistance and acid resistance is acquired.

[0027] Furthermore, the filler (D) contained in the constituent for CMP scouring pads of this invention is explained below.

The filler (D) used for <filler (D)> this invention consists of an organic filler (d1) and/or an inorganic filler (d2). First, an organic filler (d1) is explained.

[0028] Especially as a <organic filler (d1)> above-mentioned organic filler (d1), although not limited, the organic filler 0.01-20 micrometers of whose mean particle diameter measured by the Coulter counter method are 0.1-3 micrometers preferably is desirable. It is desirable for macromolecule particles, such as a silicone rubber elastic body, a fluororesin, an aramid fiber, and polystyrene resin, to be mentioned, and to use a silicone rubber elastic body preferably as such an organic filler (d1). one sort as which this organic filler (d1) is chosen from these -- or two or more sorts can be combined and it can use.

[0029] When the filler (D) used for this invention consists of an organic filler (d1), as for an organic filler (d1), it is desirable to contain in 15 - 50% of the weight of the amount preferably ten to 70% of the weight in the constituent for CMP scouring pads (100 % of the weight). By containing the organic filler (d1) of the above-mentioned particle diameter range in the above-mentioned range, flexibility is given to a CMP scouring pad and the breakage when installing in deformation of the pad after a mould and polish equipment can be prevented. Furthermore, it is possible to adjust the degree of hardness of a CMP scouring pad front face, and, thereby, the effect on the polish effectiveness by the variation in the particle size of the abrasive material used for CMP polish can be prevented.

[0030] Moreover, it is desirable to use an epoxy group content silicone rubber elastic body still more preferably as the above-mentioned silicone rubber elastic body. Specifically as an epoxy group content silicone rubber elastic body, TOREFIRU E-601 (Dow Corning Toray Silicone make) etc. is mentioned. When an epoxy group content silicone rubber elastic body contains in the constituent for CMP scouring pads, the CMP scouring pad obtained from this elastic body having the good dispersibility to the inside of a constituent is formed into low elasticity, the stress after this pad shaping can be eased by it, and the effectiveness that the flatness of this pad improves further is acquired.

[0031] Especially as a <inorganic filler (d2)> above-mentioned inorganic filler (d2), although not limited, the quality of an inorganic fiber, a non-subtlety particle, etc. are mentioned. this inorganic filler (d2) has these independent -- or it comes to be mixed As the above-mentioned quality of an inorganic fiber (d2), the quality of an inorganic fiber the diameter of fiber measured from the SEM photograph is [0.1-1 micrometer of 0.1-0.5 micrometers of 1-30 micrometers of whose fiber length] 1-20 micrometers preferably further is desirable.

[0032] It is desirable for calcium silicate, a potassium titanate whisker, a silicon carbide whisker, a glass fiber, a carbon fiber, etc. to be mentioned, among these to use calcium silicate and a potassium titanate whisker preferably as such quality of an inorganic fiber (d2). This quality of an inorganic fiber (d2) consists of one sort chosen from these, or two sorts or more.

[0033] Specifically as the above-mentioned calcium silicate, TISUMO D, TISUMO N (product made from Otsuka Chemistry), etc. are mentioned as potassium titanate whiskers, such as ZONOHAIJI and Moss Heidi (Ube Material Industries make). The filler (D) used for this invention consists of an inorganic filler (d2), and when an inorganic filler (d2) is the quality of an inorganic fiber, as for such quality of an inorganic fiber, it is desirable to contain in 10 - 50% of the weight of the amount preferably five to 70% of the weight in the constituent for CMP scouring pads (100 % of the weight). The mechanical strength of the pad for CMP polish obtained by containing the inorganic fiber in the above-mentioned diameter range of fiber and the fiber length range in the above-mentioned range can improve, and when molding shrinkage becomes low further, the breakage at the time of this pad deformation after a mould and handling can be prevented. Furthermore, the alkali resistance and acid resistance of a CMP scouring pad improve, and adjustment of surface hardness is still also attained.

[0034] Moreover, the mean particle diameter measured with the BET adsorption method has [the non-subtlety particle used as the above-mentioned inorganic filler (d2)] a ten to 1x10²nm preferably desirable non-subtlety particle ten to 1x10³nm. It is desirable to mention metallic oxides, such as a

silicon dioxide, titanium oxide, an aluminum oxide, and yttrium oxide, and a multiple oxide ultrafine particle, and for a silicon dioxide to use preferably as such a non-subtlety particle. This non-subtlety particle consists of one sort chosen from these, or two sorts or more. Specifically as the above-mentioned silicon dioxide, Nanotech (C.I. Kasei make) etc. is mentioned.

[0035] The filler (D) used for this invention consists of an inorganic filler (d2), and when an inorganic filler (d2) is a non-subtlety particle, as for such a non-subtlety particle, it is desirable to contain in 1 - 30% of the weight of the amount preferably 0.1 to 50% of the weight in the constituent for CMP scouring pads (100 % of the weight). In addition to the above-mentioned effectiveness in the case of adding an inorganic fiber by adding the non-subtlety particle of the above-mentioned particle diameter range in the above-mentioned range, since it is a particle, the surface flatness of a pad improves, and in case it is CMP polish, it becomes possible to reduce the probability to give a blemish to a wafer.

[0036] Furthermore, it sets to this invention. An inorganic filler (d2) You may consist of quality of an inorganic fiber, and a non-subtlety particle, and the quality of an inorganic fiber is 35 - 65% of the weight of an amount preferably five to 95% of the weight in that case in an inorganic filler (d2) (the total quantity of the quality of an inorganic fiber and a non-subtlety particle is 100 % of the weight). It is desirable for a non-subtlety particle to consist of 35 - 65% of the weight of an amount preferably five to 95% of the weight. Furthermore, as for the inorganic filler (d2) which consists of quality of an inorganic fiber, and a non-subtlety particle, it is desirable to contain in 20 - 50% of the weight of the amount preferably 15 to 70% of the weight in the constituent for CMP scouring pads (100 % of the weight).

[0037] By adding these inorganic fillers (d2) in the above-mentioned amount, contraction of a CMP scouring pad becomes small and flatness, alkali resistance, and acid resistance improve. Moreover, when the filler (D) used for this invention consists of the above-mentioned organic filler (d1) and the above-mentioned inorganic filler (d2), it is desirable in a filler (D) (100 % of the weight) for an organic filler (d1) to be 20 - 60% of the weight of an amount preferably five to 95% of the weight, and for the inorganic filler (d2) to contain it in 40 - 80% of the weight of the amount preferably five to 95% of the weight.

[0038] Furthermore, when a filler (D) consists of the above-mentioned organic filler (d1) and an inorganic filler (d2), it is also preferably desirable [a filler (D)] in the constituent for CMP scouring pads (100 % of the weight) to contain in 10 - 50% of the weight of the amount ten to 70% of the weight. When such a filler (D) contains in the above-mentioned range in the constituent for CMP scouring pads, the surface hardness of a CMP scouring pad, mechanical strength, deformation, and adjustment of smoothness are possible, and the presentation can be properly used suitably with the size for polish.

[0039] In <other filler> this invention, a release agent, a silane coupling agent, a flame retarder, a coloring agent, a low stress-ized agent, a filler, etc. can be added to the constituent for CMP scouring pads of this invention if needed. As the above-mentioned release agent, metallic soap, such as metal salt; zinc stearate of higher fatty acids, such as ester wax; behenic acid zinc of higher fatty acids [, such as higher-fatty-acid; carnauba wax], such as a montanoic acid, stearin acid, behenic acid, and oleic acid, zinc oleate, barium stearate, magnesium stearate, and aluminum stearate, can be mentioned, and one sort chosen from these or two sorts or more can be added.

[0040] Moreover, as the above-mentioned silane coupling agent, carbon black, a phthalocyanine, etc. can mention [a bromine-ized epoxy resin, an antimony trioxide an aluminum hydroxide etc.] butadiene rubber etc. for beta-(3, 4 epoxycyclohexyl) ethyltrimethoxysilane, gamma-glycidoxypolytrimetoxysilane, etc. as a low stress-ized agent as the above-mentioned coloring agent as the above-mentioned flame retarder.

[0041] [Constituent for CMP scouring pads] The above-mentioned bulking agent (D) ** which consists of an epoxy resin (A), a curing agent (B), a hardening accelerator (C) and (d1) an organic filler, and/or (d2) an inorganic filler contains the constituent for CMP scouring pads concerning this invention. Therefore, as a mode of the constituent for CMP scouring pads concerning this invention, the following constituents are mentioned, for example.

(1) The constituent for CMP scouring pads containing an epoxy resin (A), a curing agent (B), a hardening accelerator (C), and the bulking agent (D) that consists of an organic filler (d1).

(2) The constituent for CMP scouring pads containing an epoxy resin (A), a curing agent (B), a hardening accelerator (C), and the bulking agent (D) that consists of an inorganic filler (d2).

(3) The constituent for CMP scouring pads containing the bulking agent (D) which consists of an epoxy resin (A), a curing agent (B), a hardening accelerator (C), an organic filler (d1), and an inorganic filler (d2).

[0042] The CMP scouring pad obtained from this constituent when the constituent for CMP scouring pads concerning this invention is either of (1) - (3) and each constituent is an above-mentioned presentation rate is excellent in alkali resistance and acid resistance, further, since it can manufacture a CMP scouring pad by compression molding according to this constituent, can be cast in a short time compared with the manufacture depended on the conventional notes form, and is excellent also in the productivity of a CMP scouring pad.

[0043] [CMP scouring pad] The CMP scouring pad concerning this invention is manufactured by the following approach using the above-mentioned constituent for CMP scouring pads. Usually, thickness of a diameter is large at about 1mm, and a CMP scouring pad is manufactured by 350mm. An example (the thickness of 1.2mm, diameter of 350mm) of the CMP scouring pad of this invention is shown in drawing 2.

[0044] In such a CMP scouring pad, although the content of the constituent in the constituent for CMP scouring pads can adjust the surface hardness and flatness, in this invention, it is desirable to adjust the content of a constituent so that surface hardness may be obtained by the BIKKAZU degree of hardness and 2-40, and 20-100 micrometers of flatness preferably measured by 4-30, and the three-dimensions measuring method may be preferably obtained by 30-70 micrometers.

[0045] The [manufacture approach of a CMP scouring pad] The manufacture approach of the CMP scouring pad concerning this invention is shown hereafter. A CMP scouring pad is manufactured by carrying out compression molding of the resin tablet which consisted of resin granulation which the manufacture approach of a CMP scouring pad consists of the above-mentioned constituent for CMP scouring pads in a mould metal mold cavity, and is not heated by the RF, or this constituent for CMP scouring pads, and was heated by the RF.

[0046] The resin granulation which carries out heating kneading, cools and grinds continuously the epoxy group content compound mentioned above, a curing agent, a hardening accelerator, an organic filler and/or an inorganic filler, and the constituent for CMP scouring pads that contains the silane coupling agent further by 2 rolls after mixing or the kneader with mixers, such as a Henschel mixer and a ribbon blender, and does not specifically heat it by the RF probably is obtained. Or further, this resin granulation is tablet-sized with a tableting press, it heats by high frequency with a high-frequency-preheating machine, and a resin tablet is obtained.

[0047] Next, the resin tablet heated by the above-mentioned high frequency or the resin granulation which is not heated by high frequency is placed using the compression molding equipment shown in drawing 2 on the molding-under molding metal mold heated by 170 degrees C metal mold 61.

Furthermore, after putting the top molding metal mold 63, it compresses by performing hot press with the movable base 64, and compression molding of the pad constituent for CMP polish is carried out in the cavity section 65 between the bottom molding metal mold 61 and the top molding metal mold 63. After resin's hardening, the top molding metal mold 63 and the periphery ring 62 are removed, after cooling the hardened sheet in Ayr, it takes out and the CMP scouring pad concerning this invention is obtained.

[0048] Usually, the general manufacture approach of a CMP scouring pad heats by the RF what tablet-sized the constituent for CMP scouring pads at the room temperature, and is performed by the approach of transfer-molding. However, when manufacturing a pad by this shaping approach, in order that the gate may be needed for the product section of a manufacturing installation and the transfer pressure of a constituent may concentrate near [that] the gate, consistency variation becomes large in the manufactured pad, and the obtained CMP scouring pad is [become] easy to deform. However, according to the manufacture approach of the CMP scouring pad applied to this invention which manufactures a CMP scouring pad by compression molding using the constituent for CMP scouring

pads of this invention, the gate is not required for the product section of a manufacturing installation, and further, when a pressure joins homogeneity, the thing of the CMP scouring pad with little deformation can be obtained and carried out to the whole constituent.

[Translation done.]

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] (A) The constituent for CMP scouring pads characterized by filler ** which consists of an epoxy resin, the (B) curing agent, the (C) hardening accelerator and a (D) (d1) organic filler, and/or (d2) an inorganic filler containing.

[Claim 2] The constituent for CMP scouring pads according to claim 1 which the above-mentioned organic filler (d1) is 0.01-20 micrometers in mean particle diameter measured by the Coulter counter method, and is characterized by containing in 10 - 70% of the weight of the amount further in the constituent for CMP scouring pads (100 % of the weight).

[Claim 3] The constituent for CMP scouring pads according to claim 1 characterized by for an inorganic filler (d2) according to claim 1 consisting of quality of an inorganic fiber which is 1-30 micrometers in fiber length, and is 0.1-1 micrometer of diameters of fiber, and containing in 5 - 70% of the weight of the amount further in the constituent for CMP scouring pads (100 % of the weight).

[Claim 4] The constituent for CMP scouring pads according to claim 1 characterized by for an inorganic filler (d2) according to claim 1 consisting of a non-subtlety particle which is the mean particle diameter of ten to 1x103nm measured with the BET adsorption method, and containing in 0.1 - 50% of the weight of the amount further in the constituent for CMP scouring pads (100 % of the weight).

[Claim 5] The constituent for CMP scouring pads according to claim 1 to 4 characterized by for the above-mentioned filler (D) consisting of an organic filler (d1) and an inorganic filler (d2), and containing in 10 - 70% of the weight of the amount in the constituent for CMP scouring pads (100 % of the weight).

[Claim 6] The constituent for CMP scouring pads according to claim 1 with which the above-mentioned epoxy resin (A) is characterized by being the epoxy resin which has two or more epoxy groups in intramolecular.

[Claim 7] The constituent for CMP scouring pads according to claim 1 to 6 with which the above-mentioned curing agent (B) is characterized by being phenol novolak resin or aralkyl phenol resin.

[Claim 8] The CMP scouring pad by which it is forming-from constituent for CMP scouring pads according to claim 1 to 7 characterized.

[Claim 9] The manufacture approach of the CMP scouring pad characterized by carrying out compression molding of the resin tablet which consisted of resin granulation which consists of a constituent for CMP scouring pads according to claim 1 to 7 in a mould metal mold cavity, and is not heated by the RF, or this constituent for CMP scouring pads, and was heated by the RF.

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最終頁に続く

(54) 【発明の名称】 CMP研磨パッド用組成物、CMP研磨パッドおよびその製造方法

(57) 【要約】 (修正有)

【課題】 耐アルカリ性および耐酸性に優れたCMP研磨パッドを得ることができる組成物、および該組成物から得られたCMP研磨パッドを提供する。

【解決手段】 本発明に係るCMP研磨パッド用組成物は、(A) エポキシ樹脂、(B) 硬化剤、(C) 硬化促進剤、および (D) (d1) 有機充填材および/または (d2) 無機充填材からなる充填材、が含有されてなる。本発明のCMP研磨パッドは、該組成物からなり、かつ高周波で加熱しない樹脂顆粒、または該組成物からなり、かつ高周波で加熱した樹脂タブレットを圧縮成型する製造方法により製造される。

【特許請求の範囲】

【請求項 1】 (A) エポキシ樹脂、(B) 硬化剤、

(C) 硬化促進剤、および (D) (d1) 有機充填材および／または (d2) 無機充填材からなる充填材、が含まれていることを特徴とする CMP 研磨パッド用組成物。

【請求項 2】 上記有機充填材 (d1) が、コールターカウンタ法で測定した平均粒径 $0.01 \sim 20 \mu\text{m}$ であり、さらに CMP 研磨パッド用組成物 (100 重量%) 中に 10～70 重量%の量で含有されていることを特徴とする請求項 1 に記載の CMP 研磨パッド用組成物。

【請求項 3】 請求項 1 に記載の無機充填材 (d2) が、繊維長 $1 \sim 30 \mu\text{m}$ であり、かつ繊維径 $0.1 \sim 1 \mu\text{m}$ である無機繊維質からなり、さらに CMP 研磨パッド用組成物 (100 重量%) 中に 5～70 重量%の量で含有されていることを特徴とする請求項 1 に記載の CMP 研磨パッド用組成物。

【請求項 4】 請求項 1 に記載の無機充填材 (d2) が、BET 法で測定した平均粒径 $10 \sim 1 \times 10^3 \text{nm}$ である無機微粒子からなり、さらに CMP 研磨パッド用組成物 (100 重量%) 中に 0.1～50 重量%の量で含有されていることを特徴とする請求項 1 に記載の CMP 研磨パッド用組成物。

【請求項 5】 上記充填材 (D) が、有機充填材 (d1) および無機充填材 (d2) からなり、かつ、CMP 研磨パッド用組成物 (100 重量%) 中に 10～70 重量%の量で含有されていることを特徴とする請求項 1～4 のいずれかに記載の CMP 研磨パッド用組成物。

【請求項 6】 上記エポキシ樹脂 (A) が、分子内に 2 以上のエポキシ基を有するエポキシ樹脂であることを特徴とする請求項 1 に記載の CMP 研磨パッド用組成物。

【請求項 7】 上記硬化剤 (B) が、フェノールノボラック樹脂またはアラルキルフエノール樹脂であることを特徴とする請求項 1～6 のいずれかに記載の CMP 研磨パッド用組成物。

【請求項 8】 請求項 1～7 のいずれかに記載の CMP 研磨パッド用組成物から形成されていることを特徴とする CMP 研磨パッド。

【請求項 9】 モールド金型キャビティ内において、請求項 1～7 のいずれかに記載の CMP 研磨パッド用組成物からなり、かつ高周波で加熱しない樹脂顆粒、または該 CMP 研磨パッド用組成物からなり、かつ高周波で加熱した樹脂タブレットを圧縮成型することを特徴とする CMP 研磨パッドの製造方法。

【発明の詳細な説明】

【0001】

【発明の技術分野】 本発明は、CMP 研磨パッド用組成物、該組成物から得られる CMP 研磨パッドおよびその製造方法に関し、具体的には、半導体集積回路を製造する際のシリコンウエハ表面を平坦に研磨するのに好適な CMP 研磨パッドを得ることのできる CMP 研磨パッド

用組成物、該組成物から得られた CMP 研磨パッドおよび該パッドの製造法に関する。

【0002】

【発明の技術的背景】 最近の半導体メモリに代表される大規模集積回路 (LSI) は、年々集積化や微細化が進んでおり、それに伴い、大規模集積回路の製造技術が高密度化し、製造工程も複雑化している。さらに、半導体デバイスの積層数も増加しており、それにより、従来は問題とならなかった半導体デバイス表面の凹凸が問題となっている。つまり、半導体デバイス表面が凹凸であることにより、断線や抵抗値のばらつきなどの発生につながっている。

【0003】 また、大規模集積回路 (LSI) の集積化に伴って、ウエハ表面にマスクのパターンを形成するパターン形成技術としてリソグラフィ (投影露光) が行われているが、近年の半導体集積回路の微細化によって、露光波長が短くなり、さらに露光装置の焦点深度が非常に浅くなってきている。そのため、ウエハ表面に凹凸が存在するとマスクのパターンが解像できなくなることから、ウエハ表面の平坦化が一層求められている。

【0004】 従来からウエハ表面の平坦化技術としては、ガラスメルト法、スピノングラス法などが使用されているが、それらは主に断線を防止するためのものである。そこで、断線、抵抗値のばらつき、さらにパターンを解像できない等の問題を解消する方法として、近年、化学的機械的研磨 (Chemical Mechanical Polishing (以下、CMP ともいう。)) 技術によるウエハ表面を平坦化する方法が主流となっている。

【0005】 ウエハ表面を平坦化する CMP は図 1 に示される装置を用いて行われる。図 1 に示される CMP 装置 1 は回転する円盤 10 と、ホルダープレート 31 およびモーター 32 を有するウエハ回転装置 30 からなっており、円盤 10 には CMP 研磨パッド 20 が設置されており、CMP 研磨パッド 20 上にスラリー状の研磨剤を滴下する滴下装置 50 がついている。ウエハ 40 はホルダープレート 31 に保持され、その表面が CMP 研磨パッド 20 に接触し、さらに、モーター 32 によって回転する。CMP 研磨パッド 20 は円盤 10 と共に回転し、滴下装置 50 から該パッド 20 上に滴下された研磨剤によりウエハ 40 の表面を研磨して、ウエハ 40 表面を平坦化する。

【0006】 また、CMP は単にウエハ表面を平坦化するだけでなく、埋め込み配線 (ダマシ) を形成するためにも使用される。CMP に用いられる CMP 研磨パッドとしては、現在、発泡ポリウレタンからなるパッドが用いられている。しかしながら、このパッドは平面度が悪く、また、発泡しているポリウレタンを使用しているため、その微細な穴に研磨粉が入り込みやすく、パッドが目詰まりを起こしやすいという問題があった。

【0007】 さらに、CMP 研磨の対象となるものとし

て配線（AL、Wなど）、絶縁層（SiO₂など）の二つが挙げられる。この二つを研磨する際に用いられる研磨剤はpHが大きく異なっており、配線を研磨する場合には、pHが3程度の酸性の研磨剤を用い、絶縁層を研磨する場合には、pHが11程度のアルカリ性の研磨剤を用いる。したがって、CMP研磨パッドには、耐アルカリ性および耐酸性の両方の性能が要求される。この要求にこたえるために、エポキシ樹脂製の研磨パッドが提案されている（特開平11-138420号公報）。

【0008】しかし、このエポキシ樹脂製の研磨パッドは耐アルカリ性および耐酸性の両方の性能を十分に満たすものではなく、さらに、該研磨パッドの製造方法は、液状のCMP研磨パッド用組成物を注形し、成形する方法であるため、パッド1枚当たり5～12時間の硬化時間を要し、CMP研磨パッドの生産性が低いという問題があった。

【0009】

【発明の目的】本発明は、前述したような従来技術における問題を解決しようとするものであって、耐アルカリ性および耐酸性に優れたCMP研磨用パッドを得ることができる組成物、および、該組成物から得られたCMP研磨パッド、さらに生産性に優れた該パッドの製造方法を提供することを目的としている。

【0010】

【発明の概要】本発明に係るCMP研磨パッド用組成物は、(A)エポキシ樹脂、(B)硬化剤、(C)硬化促進剤、および(D)(d1)有機充填材および/または(d2)無機充填材からなる充填材、が含有されていることを特徴としている。上記有機充填材(d1)が、コールターカウンター法で測定した平均粒径0.01～20μmであり、さらにCMP研磨パッド用組成物(100重量%)中に10～70重量%の量で含有されていることが好ましい。

【0011】上記無機充填材(d2)が、繊維長1～30μmであり、かつ繊維径0.1～1μmである無機繊維質からなり、さらにCMP研磨パッド用組成物(100重量%)中に5～70重量%の量で含有されていることも好ましい。また、上記無機充填材(d2)が、BET法で測定した平均粒径10～1×10³nmである無機微粒子からなり、さらにCMP研磨パッド用組成物(100重量%)中に0.1～50重量%の量で含有されているこ

とが望ましい。

【0012】上記有機充填材(d1)および上記無機充填材(d2)からなる充填材(D)が、CMP研磨パッド用組成物(100重量%)中に10～70重量%の量で含有されていることも望ましい。上記エポキシ樹脂(A)が、分子中に2以上のエポキシ基を有することも望ましい。

【0013】上記硬化剤(B)がフェノールノボラック樹脂またはアラルキルフェノール樹脂であることも望ましい。本発明に係るCMP研磨パッドは、上記CMP研磨パッド用組成物から形成されていること特徴としている。本発明に係るCMP研磨パッドの製造方法は、モールド金型キャビティ内において、上記CMP研磨パッド用組成物からなり、かつ高周波で加熱しない樹脂顆粒、または上記CMP研磨パッド用組成物からなり、かつ高周波で加熱した樹脂タブレットを圧縮成型することを特徴としている。

【0014】

【発明の具体的説明】以下、本発明に係るCMP研磨パッド用組成物、CMP研磨パッドおよびその製造方法について具体的に説明する。本発明に係るCMP研磨パッド用組成物は、(A)エポキシ樹脂、(B)硬化剤、(C)硬化促進剤、および(D)(d1)有機充填材および/または(d2)無機充填材からなる充填材、が含有されている。

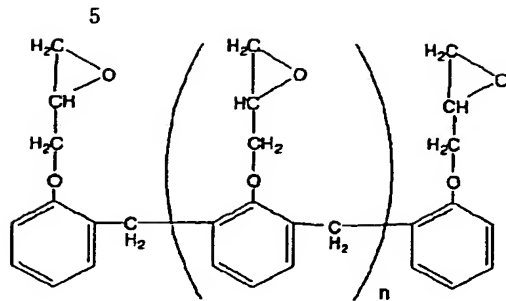
【0015】まず、エポキシ樹脂(A)について以下に説明する。

＜エポキシ樹脂(A)＞本発明に用いられるエポキシ樹脂(A)としては、特に限定されるものではないが、分子内に2以上のエポキシ基を有するエポキシ樹脂が用いられ、そのようなものとして、ノボラック型エポキシ樹脂、ナフタレン型エポキシ樹脂、ビフェニル型エポキシ樹脂、ハイドロキノン型エポキシ樹脂、ジシクロペンタジエン型エポキシ樹脂等を挙げることができ、好ましくは下記化学式に示されるノボラック型エポキシ樹脂、ナフタレン型エポキシ樹脂、ビフェニル型エポキシ樹脂、特に好ましくはノボラック型エポキシ樹脂、ナフタレン型エポキシ樹脂を用いることが望ましい。これらエポキシ樹脂は、1種または2種以上組み合わせて用いることができる。

【0016】

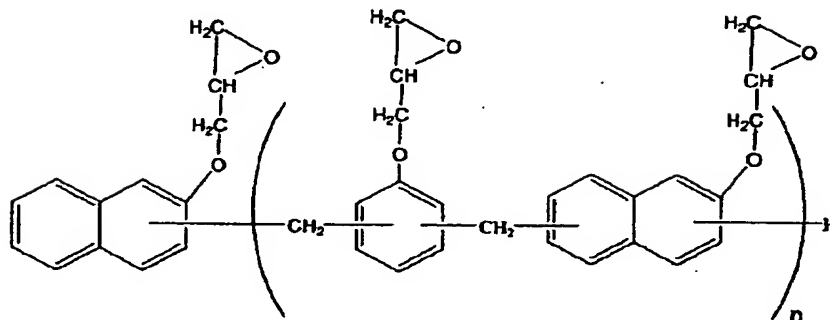
【化1】

(4)



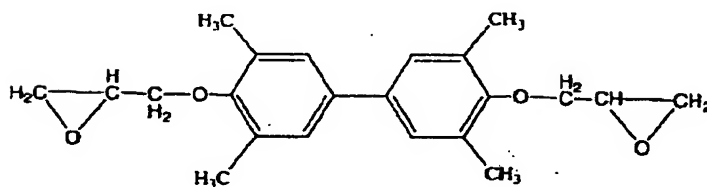
(n : 0 ~ 2)

<ノボラック型エポキシ樹脂>



(n : 0.35)

<ナフタレン型エポキシ樹脂>



<ビフェニル型エポキシ樹脂>

【0017】上記化学式に示されるノボラック型エポキシ樹脂としては、具体的には、EOCN102S、EOCN103S、EOCN104S（日本化薬（株）製）など、ナフタレン型エポキシ樹脂としては、具体的には NC7000L（日本化薬（株）製）など、ビフェニル型エポキシ樹脂としては、具体的には YX-4000（油化シェルエポキシ（株）製）などが挙げられる。

【0018】本発明に用いられるエポキシ樹脂（A）は、CMP研磨パッド用組成物（100重量%）中に、10~70重量%、好ましくは20~60重量%の量で含有していることが望ましい。次に、本発明のCMP研磨パッド用組成物に含有される硬化剤（B）について以下説明する。

【0019】<硬化剤（B）>本発明に用いられる硬化

剤（B）としては、特に限定されるものではないが、フェノールノボラック樹脂、アラルキルフェノール樹脂などが挙げられる。CMP研磨パッド用組成物にフェノールノボラック樹脂を添加した場合、耐アルカリ性、耐酸性に優れたCMP研磨パッドを得ることができ、アラルキルフェノール樹脂を添加した場合、耐アルカリ性、耐酸性に優れ、さらに低吸水性が付与されたCMP研磨パッドを得ることができる。

【0020】そのようなフェノールノボラック樹脂としては、具体的には、PN-80、PN-100（日本化薬（株）製）など、アラルキルフェノール樹脂としては、具体的には、ミレックスXLC-3L（三井化学（株）製）などが挙げられる。上記硬化剤（B）は、CMP研磨パッド用組成物（100重量%）中に、10~

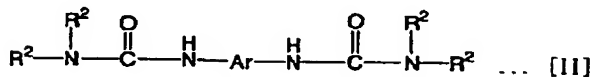
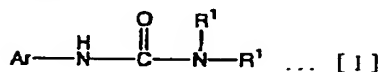
50重量%、好ましくは20～40重量%の量で含有していることが望ましい。

【0021】本発明のCMP研磨パッド用組成物中に、エポキシ樹脂(A)が上記範囲で含有され、さらに硬化剤(B)が上記範囲で含有されることにより、耐アルカリ性および耐酸性に優れたCMP研磨パッドを得ることができる。さらに、本発明のCMP研磨パッド用組成物に含有される硬化促進剤(C)について以下説明する。

【0022】＜硬化促進剤(C)＞本発明に用いられる硬化促進剤(C)としては、2-メチルイミダゾール、2-エチル-4-メチルイミダゾール、2-エチル-4-メチルイミダゾールアジン等のイミダゾール類；トリフェニルホスフィン、トリ(p-メチルフェニル)ホスフィン等の有機ホスフィン類；1,8-ジアザシクロ(5,4,0)ウンデセン-7フェノール塩、1,8-ジアザシクロ(5,4,0)ウンデセン-7フェノールノボラック塩、1,8-ジアザシクロ(5,4,0)ウンデセン-7フェノールノボラック炭酸塩などのDBU誘導体；下記式[I]、[II]で表される尿素誘導体などが挙げられる。

【0023】

【化2】



【0024】(式[I]および[II]中、R¹およびR²はアルキル基、好ましくは炭素数1～10のアルキル基、特に好ましくは炭素数1～5のアルキル基を表し、相互に同一であっても、異なってもよく、Arは置換されたアリール基、または無置換のアリール基を表す。)

本発明においては、硬化促進剤(C)として、2-メチルイミダゾール、1,8-ジアザシクロ(5,4,0)ウンデセン-7フェノールノボラック塩、上記式[II]で表される尿素誘導体を用いることが好ましい。

【0025】そのような2-メチルイミダゾールとしては、具体的には、2MZ(四国化成(株)製)など、1,8-ジアザシクロ(5,4,0)ウンデセン-7フェノールノボラック塩としては、具体的には、U-CAT-SA-831、U-CAT-SA-841(サンアプロ(株)製)など、上記式[II]で表される尿素誘導体としては、具体的には、U-CAT-3502T(サンアプロ(株)製)などが挙げられる。

【0026】これらの硬化促進剤(C)は、エポキシ樹脂100重量部に対して0.1以上20重量部以下、好ましくは0.1以上10重量部以下の量で添加される。

硬化促進剤(C)を上記配合比で添加することによって、エポキシ樹脂(A)と硬化剤(B)の反応を促進し、得られるCMP研磨パッドは耐アルカリ性および耐酸性に優れるという効果が得られる。

【0027】またさらに、本発明のCMP研磨パッド用組成物に含有される充填材(D)について以下説明する。

＜充填材(D)＞本発明に用いられる充填材(D)は、有機充填材(d1)および/または無機充填材(d2)からなる。まず、有機充填材(d1)について説明する。

【0028】＜有機充填材(d1)＞上記有機充填材(d1)としては、特に限定されるものではないが、コールターカウンタ法で測定した平均粒径が0.01～20μm、好ましくは0.1～3μmである有機充填材が望ましい。そのような有機充填材(d1)としては、シリコンゴム弾性体、フッ素樹脂、アラミド繊維、ポリスチレン樹脂などの高分子微粒子が挙げられ、好ましくはシリコンゴム弾性体を用いることが望ましい。該有機充填材(d1)は、これらから選ばれる1種または2種以上組み合わせて用いることができる。

【0029】本発明に用いられる充填材(D)が有機充填材(d1)からなる場合、有機充填材(d1)は、CMP研磨パッド用組成物(100重量%)中に、10～70重量%、好ましくは15～50重量%の量で含有していることが望ましい。上記粒子径範囲の有機充填材(d1)を上記範囲で含有することにより、CMP研磨パッドに可撓性が付与され、モールド後のパッドの変形および研磨装置に設置する時の破損を防ぐことができる。またさらに、CMP研磨パッド表面の硬度を調整することが可能であり、それにより、CMP研磨に用いられる研磨剤の粒径のバラツキによる研磨効果への影響を防止することができる。

【0030】また、上記シリコンゴム弾性体として、さらに好ましくはエポキシ基含有シリコンゴム弾性体を用いることが望ましい。エポキシ基含有シリコンゴム弾性体としては、具体的には、トレフィルE-601(東レ・ダウコーニング・シリコン(株)製)などが挙げられる。CMP研磨パッド用組成物中に、エポキシ基含有シリコンゴム弾性体が含有されることにより、該弾性体は組成物中への分散性が良好であることから得られるCMP研磨パッドは低弾性化し、それによって該パッド成形後の応力を緩和することができ、さらに該パッドの平面度が向上するという効果が得られる。

【0031】＜無機充填材(d2)＞上記無機充填材(d2)としては、特に限定されるものではないが、無機繊維質、無機微粒子などが挙げられる。該無機充填材(d2)は、これらが単独または混合されてなる。上記無機繊維質(d2)としては、SEM写真から測定した繊維径が、0.1～1μm、好ましくは0.1～0.5μm、さらに繊維長が、1～30μm、好ましくは1～20μmである無機

繊維質が望ましい。

【0032】そのような無機繊維質(d2)としては、カルシウムシリケート、チタン酸カリウムウイスカー、炭化ケイ素ウイスカー、ガラス繊維、炭素繊維などが挙げられ、このうち好ましくはカルシウムシリケート、チタン酸カリウムウイスカーを用いることが望ましい。該無機繊維質(d2)は、これらから選ばれる1種または2種以上からなる。

【0033】上記カルシウムシリケートとしては、具体的には、ゾノハイジ、モスハイジ(宇部マテリアルズ

(株)製)など、チタン酸カリウムウイスカーとしてはティスモD、ティスモN(大塚化学(株)製)などが挙げられる。本発明に用いられる充填材(D)が無機充填材(d2)からなり、かつ無機充填材(d2)が無機繊維質である場合、このような無機繊維質は、CMP研磨パッド用組成物(100重量%)中に、5~70重量%、好ましくは10~50重量%の量で含有していることが望ましい。上記繊維径範囲および繊維長範囲にある無機質繊維を上記範囲で含有することにより得られるCMP研磨パッドの機械的強度が向上し、さらに成形収縮率が低くなることにより、モールド後の該パッド変形、取扱い時の破損を防止することができる。さらに、CMP研磨パッドの耐アルカリ性および耐酸性が向上し、さらに表面硬度の調整も可能となる。

【0034】また、上記無機充填材(d2)として用いられる無機微粒子は、BET法で測定した平均粒径が $10 \sim 1 \times 10^3 \text{ nm}$ 、好ましくは $10 \sim 1 \times 10^2 \text{ nm}$ の無機微粒子が望ましい。そのような無機微粒子としては、二酸化ケイ素、酸化チタン、酸化アルミニウム、酸化イットリウムなどの金属酸化物、複合酸化物超微粒子が挙げられ、好ましくは二酸化ケイ素が用いることが望ましい。該無機微粒子は、これらから選ばれる1種または2種以上からなる。上記二酸化ケイ素としては、具体的には、ナノテック(シーアイ化成(株)製)などが挙げられる。

【0035】本発明に用いられる充填材(D)が、無機充填材(d2)からなり、かつ無機充填材(d2)が無機微粒子である場合、このような無機微粒子は、CMP研磨パッド用組成物(100重量%)中に、0.1~50重量%、好ましくは1~30重量%の量で含有していることが望ましい。上記粒子径範囲の無機微粒子を上記範囲で添加することにより、無機質繊維を添加する場合の上記効果に加え、微粒子であるためパッドの表面平面度が向上し、CMP研磨の際に、ウエハに傷をつける確率を低減することが可能となる。

【0036】さらに本発明においては、無機充填材(d2)は、無機繊維質および無機微粒子からなっているてもよく、その場合、無機充填材(d2)(無機繊維質と無機微粒子との合計量が100重量%)中に、無機繊維質が5~

微粒子が5~95重量%、好ましくは35~65重量%の量からなることが望ましい。さらに、無機繊維質および無機微粒子からなる無機充填材(d2)は、CMP研磨パッド用組成物(100重量%)中に、15~70重量%、好ましくは20~50重量%の量で含有していることが望ましい。

【0037】これらの無機充填材(d2)を上記の量で添加することにより、CMP研磨パッドの収縮率が小さくなり、平面度、耐アルカリ性および耐酸性が向上する。また、本発明に用いられる充填材(D)が、上記有機充填材(d1)と上記無機充填材(d2)とからなる場合、充填材(D)(100重量%)中に、有機充填材(d1)は5~95重量%、好ましくは20~60重量%の量で、無機充填材(d2)は5~95重量%、好ましくは40~80重量%の量で含有していることが望ましい。

【0038】またさらに、充填材(D)が上記有機充填材(d1)と無機充填材(d2)とからなる場合、CMP研磨パッド用組成物(100重量%)中に、充填材(D)は10~70重量%、好ましくは10~50重量%の量で含有していることも望ましい。このような充填材(D)がCMP研磨パッド用組成物に上記範囲で含有されることにより、CMP研磨パッドの表面硬度、機械強度、変形、平滑度の調整が可能であり、研磨対象、そのサイズによって適宜、その組成を使い分けることができる。

【0039】<その他の充填材>本発明においては、必要に応じて、離型剤、シランカップリング剤、難燃剤、着色剤、低応力化剤、充填材などを本発明のCMP研磨パッド用組成物に添加することができる。上記離型剤としては、モンタン酸、ステアリン酸、ペヘニン酸、オレイン酸などの高級脂肪酸；カルナバワックスなどの高級脂肪酸のエステルワックス；ペヘニン酸亜鉛、オレイン酸亜鉛、ステアリン酸バリウム、ステアリン酸マグネシウム、ステアリン酸アルミニウムなどの高級脂肪酸の金属塩；ジンクステアレートなどの金属石鹸を挙げることができ、これらから選ばれる1種または2種以上を添加することができる。

【0040】また、上記シランカップリング剤としては、 β -(3,4エポキシシクロヘキシル)エチルトリメトキシシラン、 γ -グリシドキシプロピルトリメトキシシランなど、上記難燃剤としては、ブrom化エポキシ樹脂、三酸化アンチモン、水酸化アルミニウムなど、上記着色剤としては、カーボンブラック、フタロシアニンなど、低応力化剤としては、ブタジエンゴムなどを挙げることができる。

【0041】[CMP研磨パッド用組成物] 本発明に係るCMP研磨パッド用組成物は、上記した、エポキシ樹脂(A)、硬化剤(B)、硬化促進剤(C)、および(d1)有機充填材および/または(d2)無機充填材からなる充填剤(D)、が含有されている。したがって、本発明に係るCMP研磨パッド用組成物の態様としては、たとえ

ば次のような組成物が挙げられる。

(1) エポキシ樹脂 (A)、硬化剤 (B)、硬化促進剤 (C)、および有機充填材 (d1) からなる充填剤 (D)、を含有している CMP 研磨パッド用組成物。

(2) エポキシ樹脂 (A)、硬化剤 (B)、硬化促進剤 (C)、および無機充填材 (d2) からなる充填剤 (D)、を含有している CMP 研磨パッド用組成物。

(3) エポキシ樹脂 (A)、硬化剤 (B)、硬化促進剤 (C)、有機充填材 (d1) および無機充填材 (d2) からなる充填剤 (D)、を含有している CMP 研磨パッド用組成物。 10

【0042】本発明に係る CMP 研磨パッド用組成物が (1) ~ (3) のいずれかであり、かつそれぞれの組成物が上述の組成割合であることにより、該組成物から得られる CMP 研磨パッドは耐アルカリ性および耐酸性に優れ、さらに、この組成物によれば、圧縮成型で CMP 研磨パッドを製造することができるため、従来の注形による製造に比べ短時間で成型可能であり、CMP 研磨パッドの生産性にも優れる。

【0043】「CMP 研磨パッド」 本発明に係る CMP 研磨パッドは、上記 CMP 研磨パッド用組成物を用いて下記の方法によって製造される。通常、CMP 研磨パッドは、厚みが 1 mm 程度で直径が大きいもので 350 mm で製造される。図 2 に、本発明の CMP 研磨パッドの一例 (厚み 1.2 mm、直径 350 mm) を示す。 20

【0044】このような CMP 研磨パッドにおいては、その表面硬度、平面度は、CMP 研磨パッド用組成物中の構成成分の含有量により調整可能であるが、本発明においては、表面硬度はビッカース硬度で 2 ~ 40、好ましくは 4 ~ 30、三次元測定法で測定される平面度は 20 ~ 100 μm 、好ましくは 30 ~ 70 μm で得られるように、構成成分の含有量を調整することが望ましい。 30

【0045】「CMP 研磨パッドの製造方法」 以下、本発明に係る CMP 研磨パッドの製造方法を示す。CMP 研磨パッドの製造方法は、モールド金型キャビティ内において、上記 CMP 研磨パッド用組成物からなり、かつ高周波で加熱しない樹脂顆粒、または該 CMP 研磨パッド用組成物からなり、かつ高周波で加熱した樹脂タブレットを圧縮成型することにより CMP 研磨パッドを製造する。

【0046】具体的には、まず、上述したエポキシ基含有化合物、硬化剤、硬化促進剤、有機充填材および/または無機充填材、さらにシランカップリング剤を含有している CMP 研磨パッド用組成物を、ヘンシェルミキサー、リボンブレンダーなどの混合機で混合後、二本ロールまたはニーダーで加熱混練りし、続いて冷却、粉碎して高周波で加熱しない樹脂顆粒を得る。または、さらに、該樹脂顆粒をタブレットマシンによりタブレット化し、さらに、高周波予熱機により高周波で加熱して樹脂 40

タブレットを得る。

【0047】次に、図 2 に示す圧縮成型装置を用い、上記高周波で加熱した樹脂タブレット、または高周波で加熱しない樹脂顆粒を、170℃に加熱された成型金型の下成型金型 61 の上に置く。さらに、上成型金型 63 をかぶせた後、可動台 64 によって加熱プレスを行い、圧縮し、下成型金型 61 と上成型金型 63 との間のキャビティ部 65 で CMP 研磨用パッド組成物を圧縮成型する。樹脂が硬化後、上成型金型 63 と外周リング 62 を外し、硬化したシートをエアで冷却した後、取り出して、本発明に係る CMP 研磨パッドを得る。

【0048】通常、一般的な CMP 研磨パッドの製造方法は、CMP 研磨パッド用組成物を室温でタブレット化したものを高周波で加熱し、トランスファー成形する方法によって行われる。しかしながら、この成形方法によってパッドを製造する場合、製造装置の製品部にゲートが必要となり、そのゲート近傍に組成物の注入圧力が集中するため、製造されたパッド内において密度バラツキが大きくなり、得られた CMP 研磨パッドは変形しやすくなる。しかしながら、本発明の CMP 研磨パッド用組成物を用い、圧縮成型によって CMP 研磨パッドを製造する本発明に係る CMP 研磨パッドの製造方法によれば、製造装置の製品部にゲートは必要でなく、さらに組成物全体に均一に圧力が加わることにより、変形の少ない CMP 研磨パッドを得ることができる。

【0049】

【発明の効果】本発明のよれば、耐アルカリ性および耐酸性に優れた CMP 研磨パッドを得ることができる組成物、および、該組成物から得られた CMP 研磨パッド、さらに生産性に優れる該パッドの製造方法を提供することができる。

【0050】

【実施例】以下、実施例に基づいて本発明をさらに具体的に説明するが、本発明はこれらの実施例に限定されるものではない。なお、実施例、比較例において得られた CMP 研磨パッドは、以下の方法に従い評価した。

パッドの平面度

パッドの平面度は、東京精密社製三次元測定機 GC-1000D を用いて測定した。測定は 23℃、53%RH の環境下で、パッド平面を 20 点接触測定することにより行った。

耐薬品性試験

研磨パッドの耐薬品性は、研磨パッドを pH12 の KOH 水溶液、pH2 の HCl/H₂O₂ 混合水溶液に 60℃ で 5 時間浸漬して研磨パッドの重量変化率：% を下記式により求め、該重量変化率から研磨パッドの耐薬品性を評価した。

【0051】

【数 1】

$$\frac{\text{浸漬後の研磨パッドの重量} - \text{浸漬前の研磨パッドの重量}}{\text{浸漬前の研磨パッドの重量}} \times 100$$

【0052】

【実施例1】ナフタレン型エポキシ樹脂（商品名；NC 7000L、日本化薬(株)製）120重量部、アラルキルフェノール樹脂（商品名；PN-80、日本化薬(株)製）94重量部、2-メチルイミダゾール（商品名；2MZ、四国化成(株)製）0.4重量部、チタン酸カリウムウイスキー〔（商品名；ティスモD、大塚化学(株)製）、平均繊維長15μm、平均繊維径0.5μm（SEM写真より測定）〕170重量部、γ-グリシドキシプロピルトリメトキシシラン（商品名；KBM-403、信越化学(株)製）0.5重量部、カルナバワックス2重量部を含有しているCMP研磨パッド用組成物をヘンシェルミキサーで混合した後、90℃に加熱した2本ロールで2分間混練した。その後、室温で冷却し、パワーミルで5mmメッシュスクリーンにて粉碎して、高周波で加熱しない樹脂顆粒を得た。この樹脂顆粒を圧縮成型金型の下成型金型の上に置き、金型温度170℃、圧縮（金型閉）時間120秒間、型締圧力35tの条件で圧縮成型し、厚さ1.2mm、直径350mmの研磨パッドを作成した。

【0053】得られた研磨パッドのパッド平面度、耐薬品性試験を上記の方法に従って評価した。結果を表1に示す。

【0054】

【実施例2】実施例1のチタン酸カリウムウイスキー170重量部をカルシウムシリケート〔（商品名；ゾノハイジ、宇部マテリアルズ(株)製）、繊維長3μm、繊維径0.3μm（SEM写真により測定）〕170重量部に40

【0055】得られた研磨パッドのパッド平面度、耐薬品性試験を上記の方法に従って評価した。結果を表1に示す。

【0056】

【実施例3】実施例1のチタン酸カリウムウイスキー170重量部に代えて、二酸化ケイ素〔（商品名；ナノテック、シーアイ化成(株)製）、平均粒子径12nm（BET法により測定）〕60重量部を添加した以外は、実施例1と同様にして研磨パッドを作成した。

【0057】得られた研磨パッドのパッド平面度、耐薬品性試験を上記の方法に従って評価した。結果を表1に

示す。

【0058】

【実施例4】実施例1のチタン酸カリウムウイスキーおよびγ-グリシドキシプロピルトリメトキシシランを無添加（0重量部）とし、シリコーンゴム〔（商品名；トレフィルE-601、東レ・ダウコーニング(株)製）、平均粒子径2μm（コールターカウンター法により測定）〕160重量部を添加した以外は実施例1と同様にして研磨パッドを作成した。

【0059】得られた研磨パッドのパッド平面度、耐薬品性試験を上記の方法に従って評価した。結果を表1に示す。

【0060】

【実施例5】実施例1のチタン酸カリウムウイスキー170重量部を40重量部とし、シリコーンゴム100重量部をさらに添加し、γ-グリシドキシプロピルトリメトキシシラン0.5重量部を0.2重量部とした以外は実施例1と同様にして研磨パッドを作成した。

【0061】得られた研磨パッドのパッド平面度、耐薬品性試験を上記の方法に従って評価した。結果を表1に示す。

【0062】

【比較例1】ナフタレン型エポキシ樹脂120重量部、アラルキルフェノール樹脂94重量部、イミダゾール0.4重量部、カルナバワックス2重量部を用い、実施例1の条件に従い研磨パッドを作成した。得られた研磨パッドのパッド平面度、耐薬品性試験を上記の方法に従って評価した。結果を表1に示す。

【0063】

【比較例2】ビスフェノールA型エポキシ樹脂（商品名；エピコート828、油化シェルエポキシ(株)製）100重量部、ジアミノジフェニルエタン24重量部からなる組成物を品川ミキサーで混合した後、図3に示した金型内に注形し、120℃で5時間加熱して硬化させた。冷却後、金型から取り出し、研磨パッドを作成した。

【0064】得られた研磨パッドのパッド平面度、耐薬品性試験を上記の方法に従って評価した。結果を表1に示す。

【0065】

【表1】

	実施例1		実施例2		実施例3		実施例4		実施例5		比較例1		比較例2	
1. 研磨パッド組成物	重量部	(重量%)	重量部	(重量%)	重量部	(重量%)	重量部	(重量%)	重量部	(重量%)	重量部	(重量%)	重量部	(重量%)
<エポキシ樹脂>														
7790型エポキシ樹脂	120.0	(31.02)	120.0	(31.02)	120.0	(43.34)	120.0	(31.88)	120.0	(33.65)	120.0	(55.45)		
ビスフェノールA型エポキシ樹脂													100.0	(80.65)
<硬化剤>														
アラキルフェノール樹脂	94.0	(24.30)	94.0	(24.30)	94.0	(33.95)	94.0	(24.97)	94.0	(26.30)	94.0	(43.44)		
ジメチルフェニルエタン													24.0	(19.65)
<硬化促進剤>														
2-メチルイソブチロール	0.4	(0.10)	0.4	(0.10)	0.4	(0.14)	0.4	(0.11)	0.4	(0.11)	0.4	(0.18)		
<無機充填材>														
チタン酸カウムイソカー	170.0	(43.83)							40.0	(11.22)				
カルシウムシリケート			170.0	(43.83)										
二酸化チタン					60.0	(21.67)								
<有機充填材>														
シリコーンゴム							160.0	(42.51)	100.0	(28.04)				
アクリルエポキシ樹脂/トリメチルシリラン	0.5	(0.13)	0.5	(0.13)	0.5	(0.18)			0.2	(0.08)				
カルナバックス	2.0	(0.52)	2.0	(0.52)	2.0	(0.72)	2.0	(0.53)	2.0	(0.56)	2.0	(0.92)		
合 計	388.9	(100.00)	388.9	(100.00)	278.9	(100.00)	378.4	(100.00)	358.8	(100.00)	216.4	(100.00)	124.0	(100.00)
2. 研磨パッドの成形条件														
2.1 成形法	圧縮成形		圧縮成形		圧縮成形		圧縮成形		圧縮成形		圧縮成形		注形	
2.1 成形時間 * 1	120秒間		120秒間		120秒間		120秒間		120秒間		120秒間		5時間	
3. 研磨パッドの特性														
3.1 パッド平面度: μm	60		85		50		50		30		500		—	
3.2 耐薬品性試験														
①重量変化率(HCl/H ₂ O ₂): %	0.8		0.6		0.7		0.5		0.6		0.9		0.9	
②重量変化率(KOH): %	0.4		0.4		0.5		0.4		0.4		0.8		0.7	

* 1: 実施例1〜比較例1までは金型が閉じている時間、比較例2は硬化するまでの時間を示す。

【図面の簡単な説明】

【図1】 図1は、CMP装置の概略図である。

【図2】 図2は、本発明のCMP研磨パッドである。

【図3】 図3は、本発明のCMP研磨パッドの製造方法に用いられる圧縮成型金型である。

【符号の説明】

- 1・・・CMP研磨装置
- 10・・・円盤
- 20・・・CMP研磨パッド
- 30・・・ウェハ回転装置

31・・・ホルダープレート

32・・・モーター

40・・・ウェハ

50・・・滴下装置

61・・・下成型金型

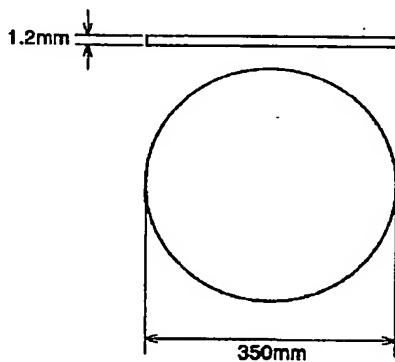
62・・・外周リング

63・・・上成型金型

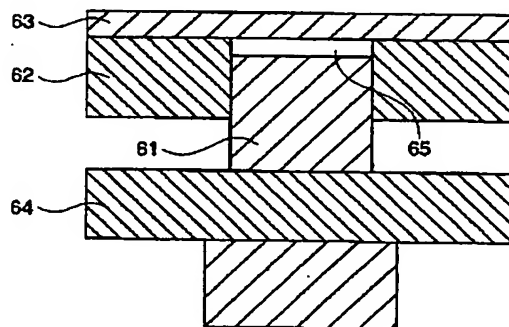
64・・・可動台

30 65・・・キャビティ部

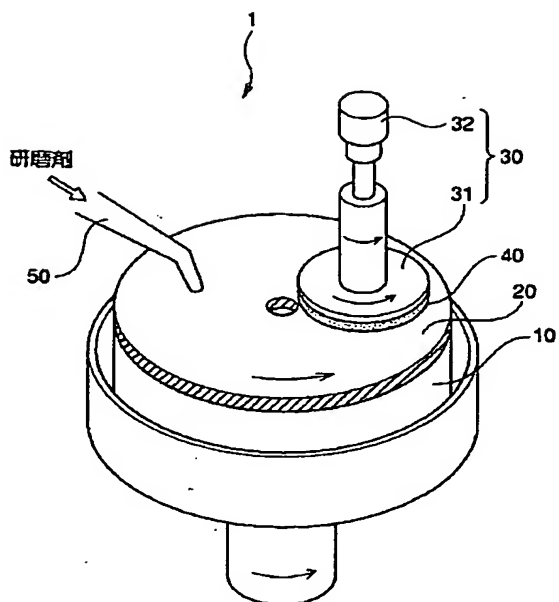
【図2】



【図3】



【図 1】



フロントページの続き

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BA01 BB03 BC07 DA06 DA07
4J002 BC033 BD123 CC04X CD03W
CD05W CD06W CF163 CP033
DA017 DE137 DJ007 DJ017
DL007 ET016 EU096 EU116
EW136 FA043 FA047 FA083
FD013 FD017 FD14X FD156
FD160 FD200 FD203 GT00